

## **Abstract**

HEIL, JOSEPH PAUL. Study and Analysis of Carbon Fiber Recycling. (Under the direction of Dr. Jerome J. Cuomo.)

To meet increasing performance demands on materials used for aerospace applications, carbon fiber composites have been increasingly turned to. With the increasing use of carbon fiber composites, also known as carbon fiber reinforced plastics (CFRPs), substantial waste is generating during manufacture as well as at the end of the service life of the composite structure. In order to reclaim the valuable carbon fiber in CFRPs and to avoid landfilling CFRPs carbon fiber recycling techniques have been developed to recover carbon fiber from CFRPs. In this work the systematic evaluation of recycled carbon fiber (RCF) from multiple material sources and multiple recycling processes has been conducted in three phases. Each phase assesses the state of the art in carbon fiber recycling. Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy, and Single Filament Tensile Testing has been used to characterize morphological, surface chemistry, and mechanical properties of recycled carbon fibers.

In the 1<sup>st</sup> phase of this work recycled carbon fibers from advanced pilot scale recycling efforts by Milled Carbon and ENEA/Karborek were evaluated. The most significant differences in fiber properties were seen between recycled standard modulus (SM) fibers and recycled intermediate modulus (IM) fibers independent of the recycling process. SM fibers recycled by Milled Carbon showed 90% retention in strength and no decrease in elastic modulus. IM T800S fibers recycled by both Milled Carbon and ENEA/Karborek showed almost no traces of residual polymer matrix, but their tensile strength was overly sensitive to gauge length showing increasingly large drops in strength with increasing gauge length.

During the 2<sup>nd</sup> phase of this study fibers from Materials Innovation Technologies and Recycled Carbon Fibre, Ltd. were studied. SM fibers from Materials Innovation Technologies showed promising test results, similar to previously studied SM fibers. In 2008 Recycled Carbon Fibre was formed to transform the carbon fiber recycling operations run by

Milled Carbon since 2003 into a commercial reality. To test process variability in Recycled Carbon Fibre's new production scale recycling furnace fibers were recovered from CFRP waste recycled on the left, center, and right side of the furnace. Fiber quality was extremely variable from one position to the other and overall fiber strength was extremely poor combined with a drop in elastic modulus never seen before.

Having comprehensive test results of single filaments of recycled carbon fiber does not provide much insight into the behavior of recycled carbon fiber composites. So in the 3<sup>rd</sup> phase of this effort sheet molding compounds (SMCs) were made from blends of virgin and recycled carbon fiber. The wetlay process was used to turn chopped fiber into nonwoven mats for use as the reinforcement component of the SMCs. Resin transfer molding was used to create flat panel SMCs from which test coupons were cut. Mechanical testing showed superior performance compared to commonly available virgin fiberglass SMCs and promising results compared to other recycled carbon fiber SMCs.

This thesis shows the evolution of recycled carbon fiber as the carbon fiber recycling community worked to boost mechanical performance and recycling capacity, handle a wide variety of CFRP materials, and demonstrate uses for recycled carbon fiber in existing products. Differences in the properties of recycled carbon fibers is explained based on the recycling feedstock, the type of carbon fiber recycled, and the interaction of these two factors with the recycling process. Understanding the changes in mechanical properties of SMCs based on the blend on recycled and virgin fibers used is the first step towards adoption of RCF into existing products and manufacturing processes.

© Copyright 2011 by Joseph Paul Heil

All Rights Reserved

Study and Analysis of Carbon Fiber Recycling

by  
Joseph Paul Heil

A thesis submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirements for the Degree  
of Master of Science

Materials Science & Engineering

Raleigh, North Carolina

2011

APPROVED BY:

---

Dr. Charles Balik  
Professor of Materials Science

---

Dr. Bhupender S. Gupta  
Professor of Textile Engineering

---

Dr. Jerome J. Cuomo  
Distinguished University Research Professor of Materials Science  
Committee Chair

## Biography

Joseph was born in April of 1987 at Wake Medical Hospital in Raleigh, NC. Much to his displeasure, at the time, he had a younger brother, Andrew, born four years later in 1991. Joseph went to Leroy Martin GT Magnet Middle School, where he was exposed to technical theatre under the direction of Judy Dove. Being very engaged academically and in the theatre arts Joseph applied to go to William G. Enloe GT/IB Center for the Humanities, Sciences, and the Arts. During his four years at Enloe Joseph took several AP classes, worked extensively with the theatre department, and also spent time with Explorer Post 512 doing event design and production in out-of-school venues. Joseph earned his Eagle Scout award in 2004 and 3 eagle palms before he turned 18.

Joseph originally intended to study electrical engineering, like his grandfather, at NCSU but was attracted to the College of Textiles through its Centennial Scholarship Program. While interviewing for the Centennial Scholarship his mom ended up guest lecturing in Dr. Cuomo's senior seminar class. After extensive discussion with Dr. Cuomo, Joseph's mom felt Joseph would also be drawn to Materials Science & Engineering. For some strange reason Joseph decided to double major in Textile Engineering and Materials Science & Engineering, completing both degrees in Spring of 2009. In January of 2006 Joseph's mom suggested he talk to Dr. Cuomo about doing undergraduate research. Taking interest in Joseph's Textile Engineering studies, Dr. Cuomo appointed him to the "Boeing Project" which analyzed Recycled Carbon Fiber. From 2006-2008 Joseph worked with Brian Allen and Myles Connor as they did their Masters work in recycled carbon fiber. From 2009 until his graduation in 2011 Joseph has led the "Boeing Project", and along the way been able to present his research locally and abroad.

## Acknowledgements

Graduate school and my time in IMST has truly been a journey I will never forget. My thanks goes out to everyone responsible for keeping IMST running especially Sarah Daniell, Dr. Roger Sanwald, and Dr. Jerry Cuomo. Dr. Cuomo took me in as a mostly average freshman and has since given me enumerable opportunities for which I am very grateful. Along the way I worked with gifted and talented students who have now moved onto life's next journey. Special mention should be made of Myles Connor and Brian Allen, whom had me as their partner in crime on the Boeing project as well as Matt King and Chris Oldham who guided me in my aspirations to conquer Atmospheric Plasma. Thanks also goes out to John Osborne, Jackson Thornton, and Brad Hartman who have helped me, teased me, and have just been fun to be around as we try to get our degrees and a job. I also need to recognize Tom Hunter for his insight into carbon fiber recycling and a few entertaining adventures out of the office. Credit also goes to Davis Litzenberger, my fellow Textile Engineer, who has been instrumental to helping me plow through the never ending testing, but also making sure I do my due diligence in analysis.

This work has been supported by the Boeing Composites Recycling Project. My gratitude also goes to Pete George, Boeing's Recycled Carbon Fiber principal investigator, for his unwavering trust in Dr. Cuomo and I.

## Table of Contents

List of Tables .....	vi
List of Figures .....	vii
List of Abbreviations .....	xii
1. Introduction to Carbon Fiber, Recycled Carbon Fiber, and Composite Concepts .....	1
1.1 What are carbon fibers and why are they used.....	3
1.2 Classification of Carbon Fibers.....	3
1.3 Processing Related Properties of PAN Based Carbon Fibers .....	6
1.4 Materials and Fiber Forms .....	16
1.5 Carbon Fiber Recycling Technologies and Methods .....	21
1.6 Composites.....	26
1.7 Key Players in Recycled Carbon Fiber “World” .....	29
1.8 Barriers to Commercialization of Recycled Carbon Fiber.....	47
2. Organization of Work To Be Presented In the Following Chapters .....	54
2.1 Background Information.....	55
3. A Comparison of Chemical, Morphological, and Mechanical Properties of Various Recycled Carbon Fibers .....	57
3.1 Abstract .....	58
3.2 Introduction .....	58
3.3 Experimental Procedure .....	60
3.4 Results & Discussion .....	63
3.5 Conclusions .....	80
4. A Comparison of Chemical, Morphological, and Mechanical Properties of Carbon Fibers Recovered From Commercial Recycling Facilities .....	82
4.1 Abstract .....	83
4.2 Introduction .....	83
4.3 Experimental Procedure .....	85

4.4	Results & Discussion .....	87
4.5	Conclusions.....	106
5.	Composite Panels Made from the Wetlay Process Using Recycled Carbon Fiber.....	108
5.1	Abstract .....	109
5.2	Introduction.....	109
5.2	Experimental .....	112
5.3	Results & Discussion .....	117
5.4	Conclusions.....	127
6.	Conclusions and Future Work .....	129
7.	References .....	131



## **List of Tables**

Table 3.1 Overview of fibers evaluated .....	60
Table 3.2 Summary of characterization techniques .....	61
Table 3.3 Fiber diameter measurements. ....	64
Table 4.1 Overview of fibers evaluated .....	85
Table 4.2 Summary of characterization techniques .....	86
Table 4.3 Fiber diameter measurements. ....	88
Table 5.1 Properties of carbon fibers considered for blending study .....	113

## List of Figures

Figure 1.1 Tensile strength of engineering materials used by the aerospace industry .....	2
Figure 1.2 Elastic modulus of engineering materials used by the aerospace industry .....	2
Figure 1.3 Schematic three-dimensional representation of structure in PAN-based high modulus carbon fibers. Fibers of lower modulus will have a more disordered structure. ....	4
Figure 1.4 The Toray T800S is an airgap wet spun fiber. Airgap wet spinning produces a smooth surface. ....	8
Figure 1.5 A) Stabilization of PAN. B) Gaseous by-products of carbon fiber production from PAN. C) Intermolecular cross-linking of stabilized PAN during carbonization through dehydration. D) Intermolecular crosslinking of stabilized PAN during carbonization through oxygen containing groups .....	10
Figure 1.6 Structure of PAN based carbon fiber during different points during .....	11
Figure 1.7 Cross linking of the cyclized sequences in PAN.....	12
Figure 1.8 Unit cell of graphite.....	13
Figure 1.9 Schematic of longitudinal structure in PAN based carbon fiber .....	13
Figure 1.10 Incorporation of graphite planes in carbon fiber .....	13
Figure 1.11 TEM of cross sectional view of graphite planes .....	13
Figure 1.12 Reynolds and Sharp mechanism of tensile failure. (a) Misoriented crystallite linking two crystallites parallel to the fibre axis. (b) Tensile stress exerted parallel to fibre axis causes layer plane rupture in direction $L^*$ , crack develops along $L$ and $L^*$ , (c) Further exertion of stress causes complete failure of misoriented crystallite. Catastrophic failure occurs if the crack exceeds the critical size in $L$ , or $L^*$ directions. ....	14
Figure 1.13 Ply Orientation.....	18
Figure 1.14 Weave Styles Used for Composites. A) Plain B) 5 Harness Satin C) 8 Harness Satin D) 2x2 Twill E) Triaxial Weave F) Three Dimensional Weaving .....	19
Figure 1.15 A) Fiber recovered from end of life material using ATI's optimized low temperature-low pressure carbon fiber recycling process B) Fracture surface of ATI's recycled carbon fiber in a polycarbonate matrix.....	32

Figure 1.16 A) Example of composite material used on Boeing 787 B) Vacuum Pyrolysis at 400°C C) Vacuum Pyrolysis at 550°C .....	33
Figure 1.17 A) Fiber from Milled Carbon/ Recycled Carbon, ltd optimized pilot scale pyrolysis carbon fiber recycling process B) Fracture Surface of fibers in figure 1.17 incorporated into a polycarbonate matrix .....	35
Figure 1.18 Fluidised Bed Recycling at University of Nottingham .....	39
Figure 1.19 Supercritical N-Propanol method for carbon fiber recycling .....	39
Figure 1.20 Crack propagation in RCF-SMC under tension. “Failure mechanisms under stable tensile crack propagation (specimen loaded; wider white arrows represent the macroscopic crack-direction): through (I) fibre–matrix interface and (II) previously-fractured fibres.” .....	44
Figure 1.21 "Failure Mechanisms of fibre-bundles under tension (wider white arrows represent the macroscopic crack-direction)” .....	45
Figure 1.22 Microstructural features during compressive loading .....	46
Figure 1.23 Compressive Failure of Recycled Carbon Fiber SMC .....	47
Figure 1.24 Importance of understanding limitations and strengths of the recycling process .....	50
Figure 1.25 Waste Generator Model. The scrap generator profits, while the recycler takes a hit giving an overall value of zero. ....	50
Figure 1.26 Recycler Model. It is the generator’s reasonability alone to prepare the waste for the recycler. ....	51
Figure 1.27 Cooperative Model. Both waste generator and recycler bear the burden of preparing the scrap but both are able to profit since the carbon fiber recovered is highly valuable. ....	52
Figure 1.28 Fiber form, processing, product relationships .....	53
Figure 3.1 A) I-MC-CTS Hexcel IM7 with heavy pitting. B) I-MC-CTS Hexcel IM7 with less visible pitting. C) Virgin Hexcel IM7 .....	66
Figure 3.2 Variable pressure SEM micrographs of T800S fibers. A) Virgin fiber B) Fiber was recycled from uncured prepreg using pyrolysis and shows evidence of pitting. ....	67

Figure 3.3 Field emission SEM micrographs for fiber sets VT800S (a) and Milled Carbon T8-MC-UTS (b). VT800S shows striations on the surface. T8-MC-UTS shows a residual surface material .....	68
Figure 3.4 A) T8-EK(L)-CT with particulate tightly bound to surface. B) T8-EK(P)-CT with evidence of residue on surface. C) T8-MC-CTS with loosely bound particulate D) Control virgin fiber with clean striated surface. ....	69
Figure 3.5 A) Virgin Toray T700G fiber. B) T7-MC-UTS recycled fiber from uncured prepreg with a non-uniform surface coating and some surface particulates.....	70
Figure 3.6 Recycled and virgin T300 carbon fibers. ....	72
Figure 3.7 Comparison of bonding types on the surface of virgin fibers. ....	73
Figure 3.8 Atomic percentages and bonding percentages for Toray T800s fibers. ....	74
Figure 3.9 Atomic percent and chemical bonding percentages for IM7 & T300 virgin and recycled fibers. ....	75
Figure 3.10 Tensile strength of virgin and recycled Cytec T300H and Hexcel AS4 fibers ..	76
Figure 3.11 Tensile strength of virgin and recycled Toray T800s carbon fibers.....	77
Figure 3.12 Elastic Modulus of T300 and AS4 fibers .....	78
Figure 3.13 Tensile modulus of virgin and recycled Toray T800S fibers. ....	78
Figure 3.14 Summary of all IFSS testing grouped by fiber type. ....	79
Figure 4.1 Means Comparison Test for Standard Modulus Fibers. ....	89
Figure 4.2 Means Comparison Test for Intermediate Modulus Fibers. ....	89
Figure 4.3 A) Virgin Cytec T-300 sample. Striations running the length of the fiber are clearly visible. B) T3-MIT-UTS-T300 fiber recovered from uncured prepreg. ....	90
Figure 4.4 A) Virgin T700G control sample. B) T7-RCFL-UTS fiber - recycled from T700G prepreg fabric.....	91
Figure 4.5 RCF12- Mostly likely AS4 or T700G fiber but exact type could not be determined to degraded condition of fiber.....	92
Figure 4.6 RCF13 Mostly likely AS4 or T700G fiber but exact type could not be determined to degraded condition of fiber.....	92
Figure 4.7 A) VCF 17- obtained by soxhlet extraction. B) RCF 14-Particualtes are clearly observable on fiber surface.....	93

Figure 4.8 A) VCF 18- obtained from Soxhlet extraction.	
B) RCF 15 recovered from prepreg. ....	94
Figure 4.9 A) VCF19-Recovered using soxhlet extraction.	
B) RCF16- Large chunks of resin remain in-between fibers. ....	95
Figure 4.10 A) Reference image for EDS analysis of RCF14.	
B) Reference image for EDS analysis of RCF15.....	96
Figure 4.11 Reference image for RCF16 EDS analysis .....	97
Figure 4.12 Atomic concentration of carbon and oxygen as measured by XPS.....	98
Figure 4.13 Atomic concentration of nitrogen, sodium, and silicon as measured by XPS ...	98
Figure 4.14 Tensile Strength of Standard Modulus Fibers. ....	100
Figure 4.15 Tensile Strength of Intermediate Modulus Fibers. ....	101
Figure 4.16 Means Comparison and Ordered Letter for Tensile Strength of IM fibers tested at the one inch gauge length. VCFT800S is the combined data of VCFs 17-19. ....	101
Figure 4.17 Means Comparison and Ordered Letter for Tensile Strength of IM fibers tested at the one quarter inch gauge length. VT800S is the combined data of VCFs 17-19.....	102
Figure 4.18 Elastic Modulus for Standard Modulus Fibers .....	104
Figure 4.19 Elastic Modulus for Intermediate Modulus Fibers .....	104
Figure 4.20 Means Comparison and Ordered Letter for Elastic Modulus of IM fibers tested at the one inch gauge length. VCFT800S is the combined data of VCFs 17-19. ....	105
Figure 4.21 Means Comparison and Ordered Letter for Elastic Modulus of IM fibers tested at the one-quarter inch gauge length. VT800S is the combined data of VCFs 17-19. ....	106
Figure 5.1 Wetlay Process for making fiber mats. Based on US Patent 5,409,573.....	111
Figure 5.2 Wetlay process run uniformity. Run 3: 100% SGL, Run 4: 50% SGL/50% R-T800S, Run 5 100% RT800S .....	115
Figure 5.3 Fiber architecture of wetlay mats .....	118
Figure 5.4. Fracture surfaces of flexure samples .....	120
Figure 5.5. Tensile strength and modulus .....	121
Figure 5.6 Comparison of tensile test data to other recycled carbon fiber composite studies .....	123
Figure 5.7 Compression testing showing both Boeing and ASTM test method results .....	124

Figure 5.8 Flexure test results (3 point bend configuration).....	125
Figure 5.9 Comparison of flexure properties to published recycled carbon fiber SMC study .....	126

## **List of Abbreviations**

3DEP	Three dimensional engineered preform
ATI	Adherent Technologies, Incorporated
BRT	Boeing Research and Technology
CF	Carbon Fiber
CFRP	Carbon Fiber Reinforced Plastic
eMIT	Materials Innovations Technologies
ICL	Imperial College London
IFSS	Interfacial Shear Strength
IM	Intermediate Modulus
IMST/NCSTU	Institute for Maintenance Science Technology at North Carolina State University
MC	Milled Carbon, Limited
RCF	Recycled Carbon Fiber
RCFL	Recycled Carbon Fiber, Limited
rCFRP	Recycled Carbon Fiber Reinforced Plastic
RTM	Resin Transfer Molding
SEM	Scanning Electron Microscopy
SFC	Single Fiber Composite Test
SM	Standard Modulus
VARTM	Vacuum Assisted Resin Transfer Molding
XPS	X-Ray Photoelectron Spectroscopy

## **1. Introduction to Carbon Fiber, Recycled Carbon Fiber, and Composite Concepts**

Carbon fibers and their composites represent a new engineering material that is growing in popularity due to its high strength & stiffness, and low density. One challenge with using this new material is what to do when the structure it made is ready to be decommissioned. Generically, the options are to throw it away, incinerate it, or recycled it. Recycling makes sense from an economic and environmental perspective; however the carbon fiber composite recycling industry is only just beginning. Engineering materials such as steel and aluminum are mature and their properties & disposal practices are well understood. Recycled carbon fiber composites will be one of the next generation engineering materials. To help understand why the use of carbon fiber is growing and why someone would want to recycle it, the mechanical properties of carbon fiber composites and other materials used in the aerospace industry are presented in Figure 1.1 and Figure 1.2. From Figure 1.1 it is clear that carbon fiber composites have a huge strength advantage over commonly used steel and aluminum alloys. Carbon fiber composites can cost about 75X as much as steel, but have only 4X the strength. However when accounting for the density of steel ( $\sim 7.85\text{g/cm}^3$ ) compare to carbon fiber composites ( $\sim 1.7\text{g/cm}^3$ ), carbon fiber composites have 18X the strength and about 3.5X the stiffness of steel. For transportation applications light-weight materials are highly valued since every pound in weight savings saves on fuel costs and every kilogram of fuel not burned saves 3kg of CO<sub>2</sub> from being emitted. The fiberglass composite shown in Figure 1.1 has a respectable strength and is also fairly light weight so its specific strength remains high. Figure 1.2 shows a comparison of elastic moduli (stiffness) for the same materials shown in Figure 1.1. For fiberglass composites, steel alloys, and aluminum alloys the specific modulus is very similar and is only a quarter of that offered by carbon fiber composites. Unadjusted for density the modulus of steel is higher than that of carbon fiber, but steel being 5x the weight of carbon fiber composites limits its attractiveness. The mechanical properties and cost figures presented here were taken from an introductory engineering text “Materials Science & Engineering: An Introduction” [1].



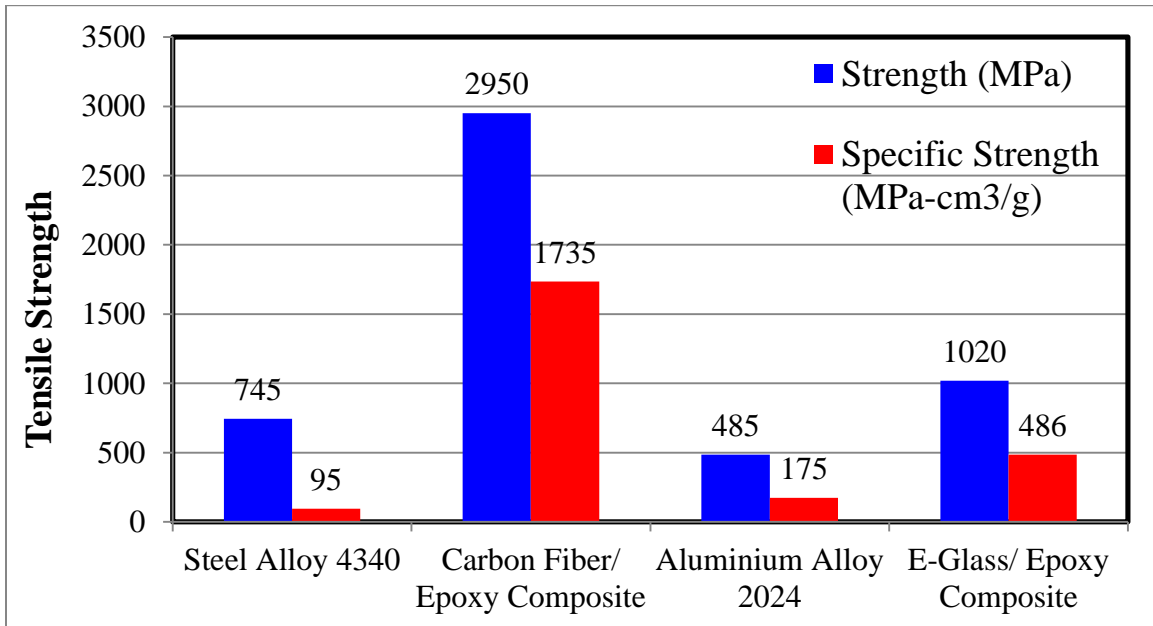


Figure 1.1 Tensile strength of engineering materials used by the aerospace industry

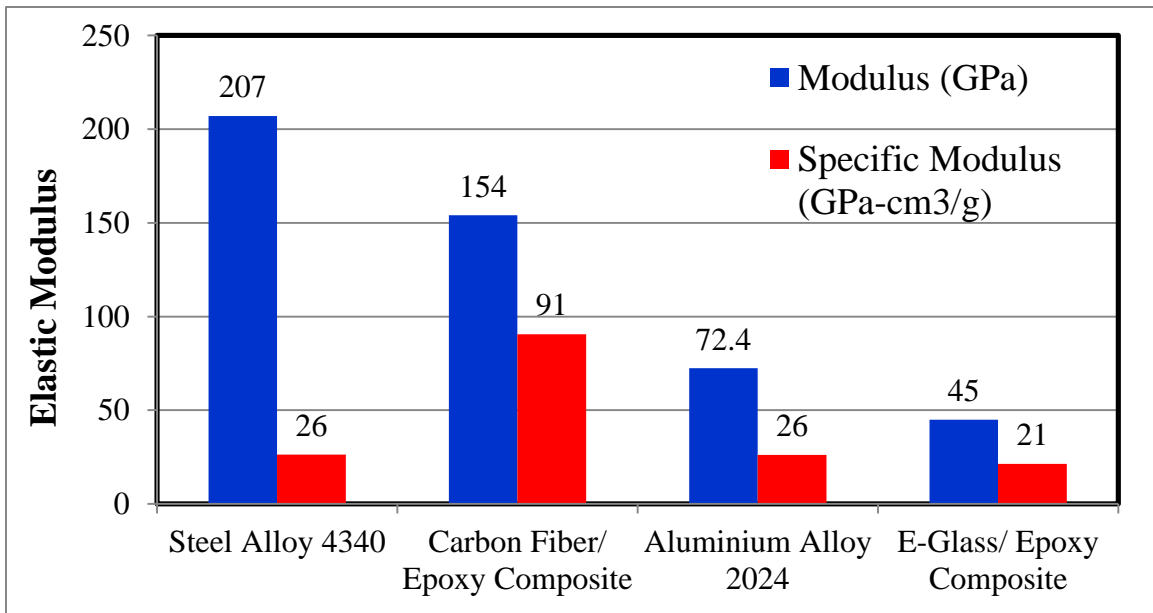


Figure 1.2 Elastic modulus of engineering materials used by the aerospace industry

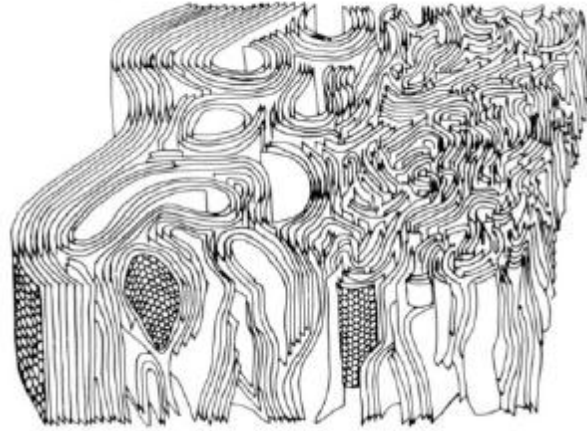
## **1.1 What are carbon fibers and why are they used**

Carbon fibers take advantage of the strong C-C bond to produce a material that is strong and lightweight. Carbon fibers get their name from their material composition, being at least 99% carbon, and their functional form, thin long cylinders much like traditional textile fibers such as cotton and polyester. Thomas Edison's quest to make a filament for his incandescent lamp resulted in the first "carbon fiber". Edison's carbon fiber did not bear much resemblance to the carbon fibers used today for highly demanding applications such as structures for air and space craft or in markets such as consumer goods sports equipment where their use is a mix of functionality and for show. However Edison's carbon fiber did demonstrate the ability to take a generic material, such as rayon, and turn it into a material with impressive strength and electrical & thermal conductivity. The impressive properties of carbon fiber can be attributed to their underlying carbonaceous structure. During the 1970's Union Carbide (today the carbon fiber production business formerly operated by Union Carbide is owned & operated by Cytec Industries) [2] purchased began developing high strength carbon fibers that have evolved into today's carbon fibers; used for enumerable consumer, commercial, and military needs. Carbon fibers are favored for their high strength, high stiffness, low reactivity, low density, and strength at higher temperatures. Carbon fibers are also used for their lubricating properties, high electrical and thermal conductivity, and low coefficient of thermal expansion (CTE). The disadvantages of carbon fiber are their high cost and their brittle character. Carbon fiber is an all-encompassing term for polymeric based carbon fibers and for pitch based carbon fibers which are stiffer and have higher thermal stability in comparison to polymeric based carbon fibers.

## **1.2 Classification of Carbon Fibers**

In the early days of the carbon fiber industry carbon and graphite fibers were interchangeably used to describe polymer based carbon fibers. However significant differences between polymer precursor carbon fibers and pitch precursor carbon fibers are found in their crystal structure and other physical properties. For example polymer precursor

carbon fibers are 93% - 95% carbon, while pitch based carbon fibers are 99+% carbon. The commonly accepted structure of carbon fibers as proposed by Johnson [3] is sheets of graphite bent around the C-axis of the fiber (Figure 1.3). In contrast, graphite fibers, are considered to have sheets of graphite stacked along the C-axis of the fiber creating a much higher crystallinity (~80%) and modulus ( $> 365\text{GPa}$ ).



**Figure 1.3 Schematic three-dimensional representation of structure in PAN-based high modulus carbon fibers. Fibers of lower modulus will have a more disordered structure. [3]**

The most universal classifying attribute of carbon fibers are their elastic modulus. The elastic modulus of a material describes its stiffness, or resistance to deformation. A more scientific definition of elastic modulus is that the elastic modulus is a measure of the force needed to displace a plane of atoms by once lattice space [4]. Working from this definition, both the structure and chemistry of a material play a role in establishing the elastic modulus of a material. Carbon fibers are commonly available in three different ranges of elastic modulus, each having increasingly higher carbon content. Standard modulus (SM) carbon fibers have an elastic modulus in the range of  $30\text{-}35 \times 10^6$  psi. A few products of this type of fiber are sigrafil C30, Hexcel AS4, Toray T700, and Cytec T300H. Intermediate modulus (IM) carbon fibers have an elastic modulus in the range of  $50\text{-}55 \times 10^6$  psi. Two examples this type of fiber are Toray T800S and Hexcel IM7. High modulus carbon fibers have an elastic

modulus in the range of  $70\text{--}75 \times 10^6$  psi. A few products of this type of fiber are HR-40 and M55J as polyacrylonitrile based fibers and Thornal P-55 as pitch based fiber. Standard modulus fibers are used for consumer goods such as sports equipment, marine craft, and automobiles. Carbon fiber comes in various grades of quality which is mostly controlled by precursor quality. High grades of both SM and IM fibers are used in the commercial aerospace market, while HM fibers are in limited use for applications needing exceptionally high stiffness at a low weight. Standard modulus fibers will generally have a fiber diameter of  $7\mu\text{m}$  which is a quick and easy way to distinguish them from IM fibers which typically have diameters of  $5\mu\text{m}$ . Other classifications of carbon fibers can be from their precursor material, spinning technology, and strength.

Carbon fiber precursor material is the material that is oxidized, carbonized, and graphitized to create carbon fiber. Selection of a suitable precursor is based on cost, carbon content, processability, and ability to form the sheets of carbon that make up the atomic structure of carbon fibers. The three most commonly known precursors are: Rayon, Polyacrylonitrile (PAN) and pitch. PAN and pitch are the most commonly used. Rayon was used to make first-generation carbon fibers, and is not common now due to lack of rayon production. Rayon is produced from naturally occurring cellulosic polymers, but is manufactured in the form of regenerated cellulose. Solvents used for manufacture of regenerated cellulose are harmful to the environment and have largely contributed to the lack of rayon production, especially in the textile industry.

Polyacrylonitrile is the most common precursor material due to low production costs and good physical properties. High purity PAN is the precursor most commonly used for aerospace grade carbon fiber. PAN is copolymerized to increase processability as well as to help control physical properties of the final product. Pitch, as a high molecular weight byproduct of petroleum distillation, naturally has highest carbon content of current precursors. The high molecular weight of pitch precursors makes them the most well suited for high modulus-high strength carbon fibers. As the demand and cost of carbon fiber has increased there is an interest in “low cost” carbon fiber derived from alternative precursors, of which lignin is the most promising. Price and performance goals for low cost carbon fiber are set based on needs for automotive and ground transportation applications. Low cost

carbon fiber has reduced mechanical performance compared to PAN and pitch based carbon fibers, but offers the potential for an inexpensive domestic supply.

### **1.3 Processing Related Properties of PAN Based Carbon Fibers**

Carbon fibers are highly valued for their high strength light weight properties and are increasingly being used in composite structures both commercially and industrially. Most of the carbon fiber manufacturing is done in Japan because of the availability of raw materials. The United States has Cytec Industries and Hexcel Corporation as local manufacturers of high grade carbon fiber used for military and aerospace applications. There are additional manufacturers of carbon fiber in the United States i.e. Zoltex, Carbon Fiber Technology, Mitsubishi Rayon America, Toho Tenax America, but since their precursor material is made abroad the Department of Defense (DOD) does not permit the use of those carbon fibers in DOD programs [2]. Although not a true manufacturing facility, Oak Ridge National Lab in conjunction with the Department of Energy has developed methods to produce low-grade carbon fiber using a variety of raw materials as well as innovative manufacturing technologies. Carbon fiber is >90% carbon and can be made from a variety of sources depending on the desired end properties and available manufacturing technologies. Commercially available carbon fiber is produced from pitch, cellulosic polymers, or PAN. Pitch fibers are extremely stiff and brittle, while carbon fiber from cellulosic precursors is relatively inferior in mechanical properties compared to pitch or PAN. PAN based precursor carbon fibers offer the widest range of properties as well as a relatively high yield [5]. The primary drawbacks to PAN are its expense and difficulty of processing. The primary steps in carbon fiber production from PAN are: spinning, stabilization, carbonization, and graphitization.

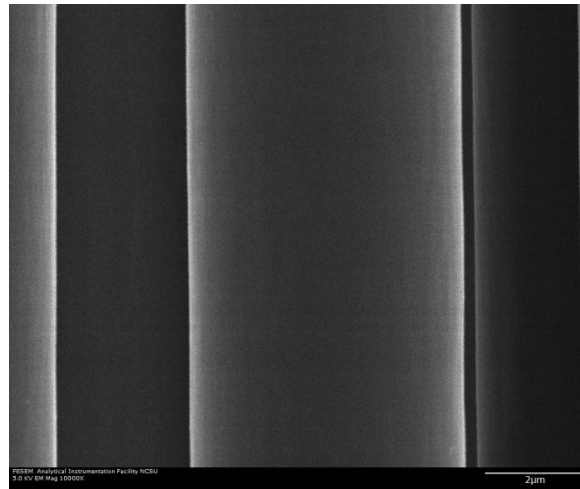
The strong polar interactions in PAN make the polymer difficult to impossible to melt process, and thus spinning is accomplished primarily by dry spinning, wet spinning, and dry-jet wet spinning. Dry spinning extrudes the PAN polymer solution through a spinneret using a volatile organic solvent kept hot by a circulating hot gas environment. Wet spinning pulls the PAN polymer solution through a coagulation bath. The bath precipitates the polymer out

of the solvent allowing the polymer solution to be drawn as a fiber. Although the processes to make carbon fiber through melt spinning have not been qualified for military use there is a considerable effort to make melt processing an inexpensive and environmentally friendly method of carbon fiber production. Melt spinning is made possible through the use of a hydrating solvent (often water or water and polyethylene glycol-PEG) that disrupts the strong polar interactions between nitrile groups enough to lower the materials melting point and melting energy [6]. The drawback to melt spinning is poorer mechanical properties resulting from internal voids and surface defects. Advantages of melt spinning are: a high degree of control over a variety of cross sectional shapes, that allow for more surface area than traditional circular cross sections, and the use of non-toxic solvents. A hybrid of wet spinning and dry spinning is dry-jet spinning. Dry-jet wet spinning extrudes the polymer precursor/ solvent solution through a spinneret as done in wet spinning but then passes it through a short air gap prior to being drawn through the coagulation bath. The resulting surface texture of a dry-jet wet spun fiber is extremely smooth such as the fiber seen in Figure 1.4. Dry-jet wet spinning is superior in that it allows for greater control of non-circular cross section shape, allows a higher spin rate, higher solids contents, and results in better mechanical properties than dry or wet spinning.

The more standard wet spinning uses 10-25% polymer content within a solvent that is passed through a block of spinnerets creating thousands of microscopic filaments which are then pulled through the coagulating bath to get PAN in the form of a fiber that is suitable for the extensive heat treatments needed to produce carbon fiber. The coagulation bath is a mixture of the solvent used to dissolve PAN and water. Higher water contents result in more rapid coagulation as does a higher bath temperature. However the high coagulation rate can result in many surface irregularities, a high pore density, and the formation of a skin-core structure [7]. In order to prepare fibers that can easily be stretched to orient the polymer chains; lower bath temperature and higher solvent contents are used. This combination results in the fiber being in a gel state where the solvent serves to disrupt the attractive forces of the PAN molecules, namely the dipole – dipole interaction of nitrile groups between chains that are strong enough to prohibit melt processing. A series of coagulating baths with different solvent temperatures and solvent concentrations are used to incrementally stretch

the fiber before passing through an oven set around 100°C which allows a stretching factor of fourteen compared to draw ratios of two and a half during the coagulation baths.

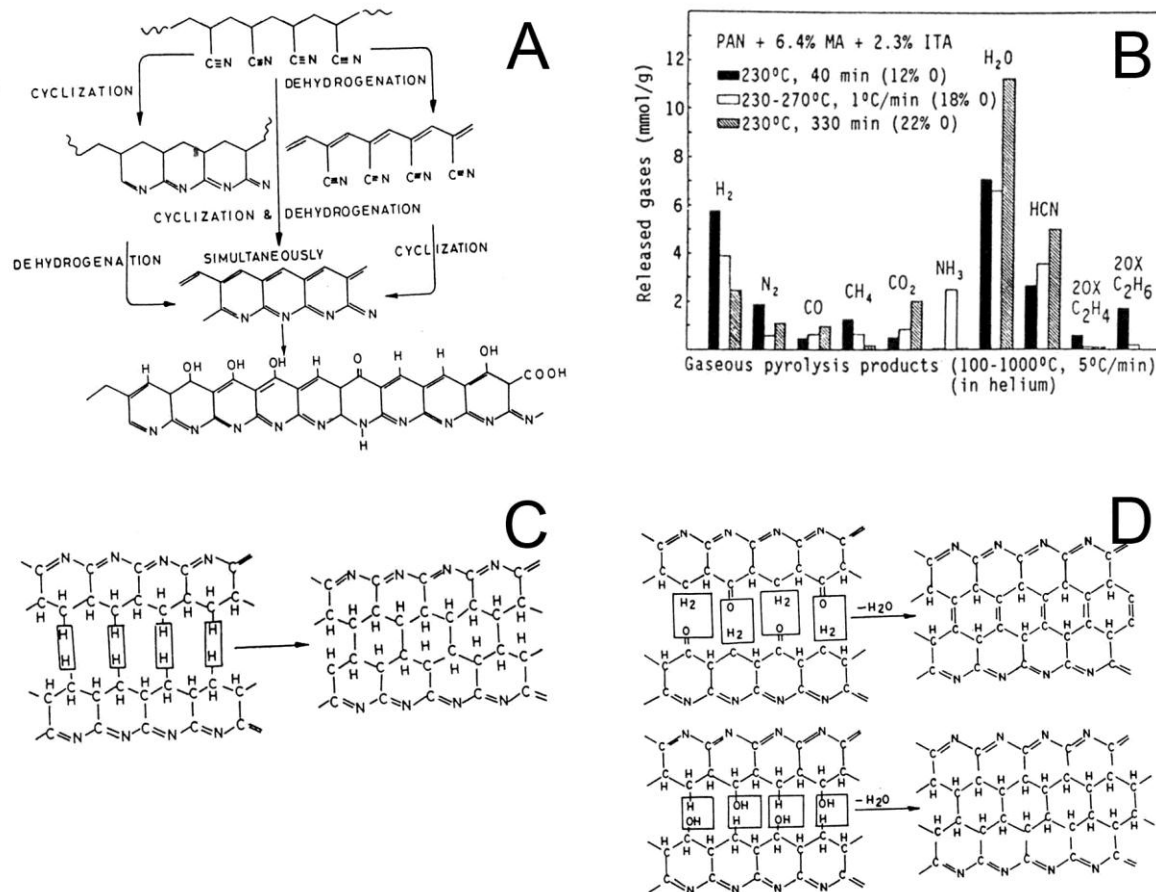
Wet spinning still has industrial appeal because it can produce more filaments at once than dry-jet wet spinning. When control over cross sectional shape is desired wet spinning is not used. When the polymer solution passes through the coagulation bath it collapses to precipitate a PAN fiber with a much lower concentration of solvent trapped in the structure. Lower polymer concentrations and bath temperatures result in more collapse and less control over cross sectional shape. During stabilization and carbonization fibers with a non-circular cross-section have better heat flux stabilization which reduces chain scission and weight loss resulting in a higher tensile strength and elastic modulus. Clearly there are many tradeoffs in spinning carbon fibers, and depending on the intended use of the fiber one set of advantages / disadvantages may weigh more heavily in making a decision on how the processing line should be adjusted. Regardless of the method of spinning after a pre-stabilization heat and draw, the fibers are ready to move onto the stabilization stage which is a series of ovens designed to stretch the fiber under increasingly higher temperature up to 300°C in an oxidative environment.



**Figure 1.4 The Toray T800S is an airgap wet spun fiber. Airgap wet spinning produces a smooth surface.**

Stabilization is used to prepare the polymer structure for the aggressive heating experienced during oxidation and carbonization. Stabilization introduces oxygen in the polymer structure of PAN as well stretches the polymer fiber to increase molecular orientation along the fiber axis. The oxygen containing groups help develop the ladder and cyclic structure that form during stabilization and carbonization [7]. About 25% shrinkage can be attributed to dehydrogenation (Figure 1.5B), evolution of hydrogenated gasses (Figure 1.5B), and conjugation cross linking of the nitrile groups (Figure 1.5A). Shrinkage occurs due to entropic effects and chemical reactions. Entropic shrinkage induced by polymer chain alignment is dominant below 200°C, while the chemical reaction creating the cyclic structure is dominant above 200°C, but is sensitive to heating rate.

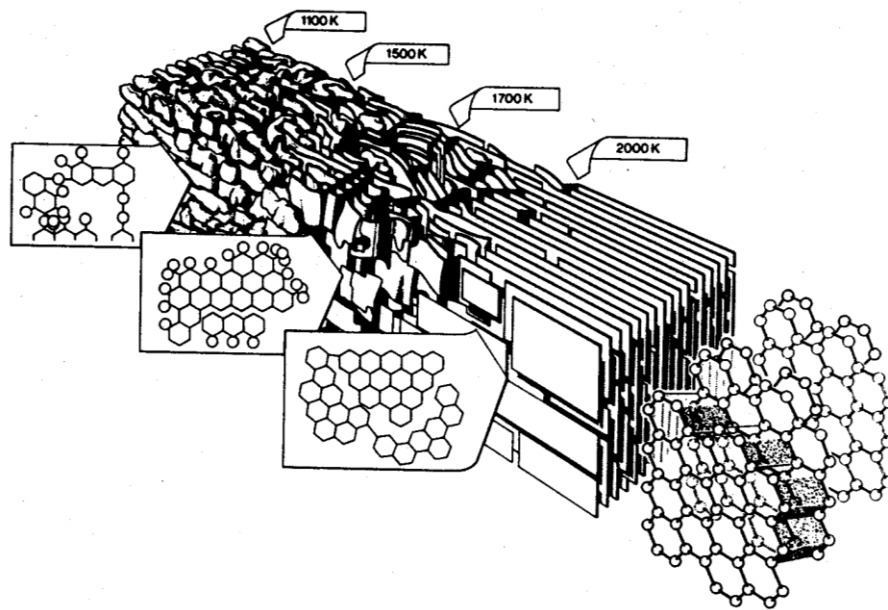




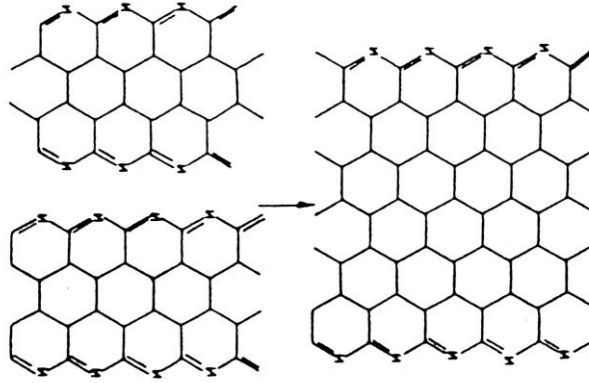
**Figure 1.5 A) Stabilization of PAN [7]. B) Gaseous by-products of carbon fiber production from PAN. [8] C) Intermolecular cross-linking of stabilized PAN during carbonization through dehydration. [7] D) Intermolecular crosslinking of stabilized PAN during carbonization through oxygen containing groups [7]**

Carbonization takes place in an inert atmosphere at temperatures of 300°C to 1500°C. Mechanical properties and yield after the carbonization stage are extremely sensitive to the comonomer content in PAN. Increased comonomer concentration increases mechanical properties, decreases time needed for stabilization, but decreases polymer yield. Drastic changes in color from white to yellow/ reddish brown, to black and also a large increase in density occurs during carbonization as a result of the formation of a cyclic structure [8]. Formation of the cyclic structure is shown in Figure 1.5C. Further evolution of gasses such as water vapor, ammonia, hydrogen cyanide, carbon monoxide, carbon dioxide,

nitrogen, and hydrogen results in a fifty weight-percent loss of the fiber (Figure 1.5D). The maximum rate of nitrogen evolution happens around 900°C. Carbonization begins with slow heating rates and keeps the overall temperature below 600°C to avoid pores and surface irregularities. At higher temperatures and faster heating rates the intermolecular cross-linking and cyclized sections coalesce by cross-linking into a graphitic structure [7]. Nitrogen is very persistent and, therefore, temperatures of 1000°C to 1500°C are used to drive out lingering nitrogen. Graphitization is an optional step in the production of carbon fiber. Fibers that require extremely high stiffness or tensile strength go through the graphitization process although at great monetary expense and a reduction in fiber elasticity. Graphitization is carried out in inert atmospheres from 1500°C to as high as 3000°C. Nitrogen is used up until 2000°C, but above 2000°C carbon and nitrogen react to form the toxic cyanogen [7]. Above 2000°C helium is used. Crystallite size and orientation are fine-tuned during graphitization. A model of carbon fiber structure during carbonization and graphitization is shown Figure 1.6.



**Figure 1.6 Structure of PAN based carbon fiber during different points during carbonization and graphitization [5]**



**Figure 1.7 Cross linking of the cyclized sequences in PAN fiber during carbonization [7]**

The tensile strength of carbon fibers has been correlated to their structural arrangement and defects by D.J. Johnson. According to Johnson the theoretical tensile strength of a material can be evaluated using the Orowan-Polamyi equation:  $\sigma = \frac{E\gamma_a^{1/2}}{a}$  where E is young's modulus,  $\gamma_a$  is the surface energy, and  $a$  is the interplanar spacing [3]. The surface energy is difficult to measure, the structure of carbon fiber is not one hundred percent known or agreed upon, and the Orowan-Polamyi equation is the theoretical strength so the presence of defects must be accounted for. Using the well-known Griffith criteria:

$\sigma^2 = \frac{2E\gamma_a}{\pi C}$  [9] Johnson theorizes the tensile strength of carbon fibers can be described based on crack size,  $C$ , young's modulus, and the surface energy of a graphite whisker,  $\gamma_a = 4.2\text{J/m}^2$ . For intermediate modulus fibers the critical crack size is 126nm, while for fibers with a high strain to failure, the critical crack size is 250nm. Stronger fibers have a smaller critical crack size and are more vulnerable to processing defects. Carbon fiber is composed of turbostratic (no 3D arrangement) carbon so the structure is hard to resolve using x-ray techniques, a promising description of the structure uses graphite planes as the fundamental building blocks (Figure 1.10). The unit cell of graphite is shown in Figure 1.8. These unit cells do not stack perfectly but rather form the interlocking ribbon structures seen in Figure 1.9. This

structure then forms the crumpled sheets in Figure 1.3. The sheets do not form perfectly against one another and create voids in the structure of the carbon fiber.

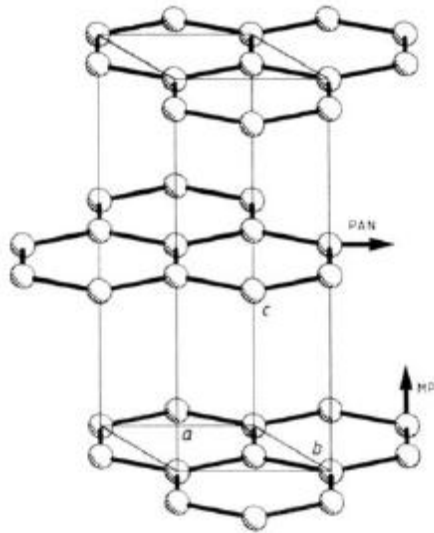


Figure 1.8 Unit cell of graphite [3]

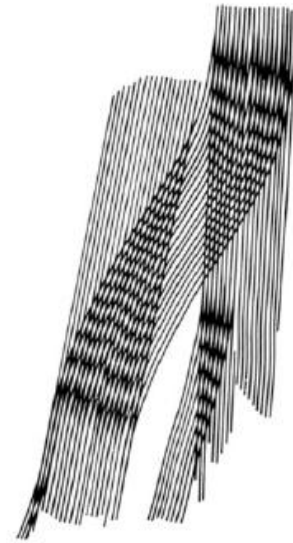


Figure 1.9 Schematic of longitudinal structure in PAN based carbon fiber [3]

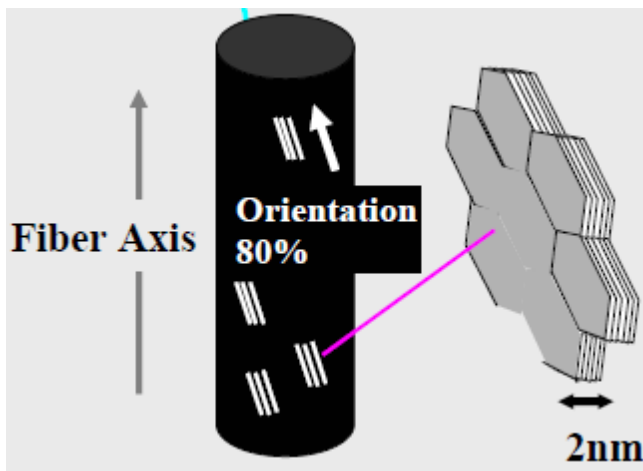


Figure 1.10 Incorporation of graphite planes in carbon fiber [10]

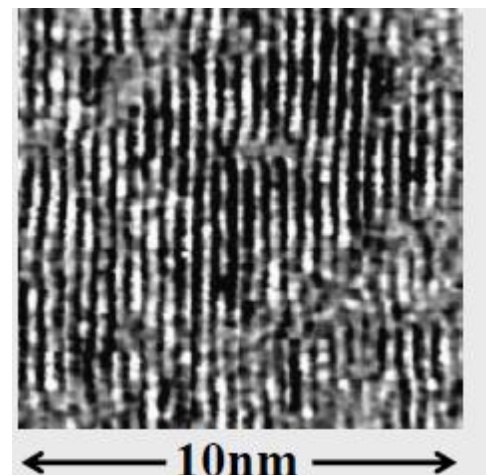


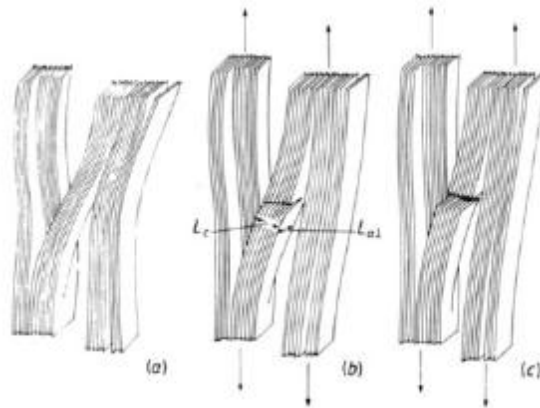
Figure 1.11 TEM of cross sectional view of graphite planes [10]

The three-dimensional interlocking of the layer planes in Figure 1.3 encloses sharp edge voids. Fewer voids will result in fibers with a higher elastic modulus. Planes close to

the outer surface of the carbon fiber are primarily parallel while planes closer to the core can be folded up to  $180^\circ$  which would give a hairpin effect. Failure mechanisms of carbon fibers cannot be explained using dislocation theory; instead they are described with respect to the unbending of curved ribbons, yielding via local shear deformation, and slippage [11]. No simple relationship exists between flaw size, fiber strength, and surface energy that would conform to failure theories for traditional solid material such as metals and ceramics. Instead the tensile failure mechanism is based on crystallite shear limit. Crystallites are weakest in shear on basal planes. When a tensile stress is applied to misoriented crystallites; they build up shear stress. Perfect solids can release this strain energy via cracking, but carbon fibers must release this energy through the rupture of basal planes. The rupture of a basal plane can cause a crack to form and propagate across and through planes (Figure 1.12). One of two criteria must be met for the described failure to happen [3,11].

Condition 1. Crystallite size in propagation direction must be greater than critical flaw size.

Condition 2. Crystallite must be sufficiently continuous to its neighbors such that a crack can propagate across surfaces.



**Figure 1.12 Reynolds and Sharp mechanism of tensile failure. (a) Misoriented crystallite linking two crystallites parallel to the fibre axis. (b) Tensile stress exerted parallel to fibre axis causes layer plane rupture in direction  $L^*$ , crack develops along  $LaI$  and  $L$ , (c) Further exertion of stress causes complete failure of misoriented crystallite. Catastrophic failure occurs if the crack exceeds the critical size in  $L$ , or  $L^*$  directions. [3]**

Condition 1 is rarely met. Condition 2 is satisfied in regions of high crystallinity and misorientation around defects. Pulling fibers, immersed in glycerol, to induce tensile failure allowed experimental examination of fracture surfaces with SEM and TEM. Internal flaws that did not fail had walls containing crystallites arranged mainly parallel to the fiber axis. Flaws that did fail contained highly misoriented crystallites or the continuity of crystallites cause condition 1 to be met. Dasilva and Johnson [12] explored tensile and flexure deformation and found the mechanism of tensile failure proposed by Reynolds and Sharp could not be expanded to explain flexure failure.

Dasilva and Johnson used the knot test to cause fibers to fail simultaneously under tension and flexure. They found little evidence that flaws were present in the fracture surfaces and concluded that fine structure accounted for differences in flexibility and brittleness. Upon examining the fracture surfaces of intermediate modulus (IM) and standard modulus (SM) fibers differences in fracture topology were observed. IM fibers had a rough striated fracture surface; smooth regions failed under tension while corrugated areas failed under compression. SM fibers had smooth surfaces where regions failed under compression, rough surface for regions that failed under tensile stress, and a deeply corrugated transmission zone. The transition zone was probably under conditions of maximum shear stress [3]. Under the conditions of the knot test more misorientation was introduced than in a simple tension test. Based on the work by Reynolds and Sharp as well as by Dasilva and Johnson; there exists a relationship between tensile strength and void content, but crystalline walls arising during carbonization and graphitization that enclose void space is the primary strength limiting factor. An ideal carbon fiber will have no gross flaws, a well developed crystalline void structure, and layer planes will be highly oriented and well interlinked.

Due to the confidential nature of carbon fiber production and the difficulty involved in examining carbon fiber structure there are many competing and incomplete explanations that relate processing conditions to structure and then structure to physical properties. The link between processing and structure can be more thoroughly understood by considering that fundamentals regarding molecular orientation, heat flux, and cross-linking are well understood and characterized. Strength limiting mechanisms are strongly linked to the purity of the polymer precursor; while creating different ranges of elastic modulus and tensile

strength is a “simple” matter of changing dwell times, temperatures, and draw ratios during carbonization and graphitization [13].

## **1.4 Materials and Fiber Forms**

Carbon fiber comes in a wide variety of forms that match the many ways of taking carbon fiber and turning it into a composite. The process to make a single carbon fiber filament is described in great detail in section 1.3, but it is important to understand the material forms that are commonly worked with to create composites. In a hierarchical order: thousands of carbon fiber filaments are bundled together to create a tow, tows are woven into fabrics or used on their own such as in filament winding and braiding, and fabric is often turned into prepreg.

### **1.4.1 Tow**

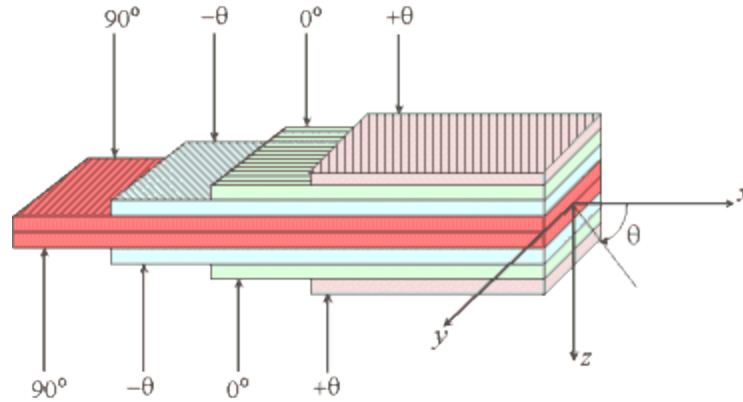
As part of the spinning process thousands of spinnerets (holes) are arranged in a tight packed configuration so that thousands of filaments are spun in close proximity to each other. Very precise mechanical methods are used to separate these filaments during oxidation, carbonization, graphitization and then to bring them back together to form a tow which is then wound onto a bobbin in a process called packaging. Just as cotton fibers are spun into a yarn to create a usable product, tows represent the most basic usable form of carbon fiber. The size of a tow is measured by the number of filaments in it. Common sizes range from 3,000-12,000 filaments which would then be called 3k tows and 12k tows. Another reason for creating tows is to average out the weaknesses in any single filament. With a small number of filaments any imperfection in a single filament will noticeably limit the strength of those few filaments, but a few imperfections among thousands of filaments will not have a significant negative effect. The arrangement of thousands of filaments into a tow also allows a load to be distributed among many filaments and allows for a load to be redistributed if a filament fails. Spools of tow may be used in composite molding processes using short fiber reinforcement, since having a continuous line of carbon fiber makes it quick and easy to chop fibers into precise lengths. Carbon fiber in the form of tows is also used in filament winding

and braiding where the architecture of the reinforcements needs to be controlled at the size scale of a tow, and not the size of a piece of fabric.

### 1.4.2 Fabric & Weave Styles

Fabric is the next processing step of carbon fiber after it's been made into tows. Carbon fiber fabric is woven from tows using the same conventional weaving technology and processes used by the textile industry for hundreds of years. Fabric is useful since it covers large areas and is easily transported. Fabric offers the opportunity for a composite to meet multiple design criteria at once. Layer by layer construction can be used to emphasize a certain property in a specific direction. Being able to emphasize strength and stiffness anisotropically cuts down on the amount of material needed to withstand the forces encountered during use of the composite compared to an isotropic material such as metals. To offer such a high degree of design customization fabric comes in different styles, at different weights, and using different types of carbon fiber. An example layup is shown in Figure 1.13. Each layer, or ply, can be layed up in a different direction with respect to the laminate and additionally, each ply can be of a different weave style as discussed later. Figure 1.13 shows 8-plys oriented in four different directions which are denoted as  $0^\circ$ ,  $90^\circ$ ,  $+\theta$  and  $-\theta$ . These directions are labeled in reference to the orientation of the laminate which is indicated by the XYZ axis system. The orientation of the warp yarns within each ply relative to the laminate's axis determines the orientation of each ply. Warp yarns running parallel to the X-axis are oriented at  $0^\circ$  with respect to the laminate and thus that ply would be a  $0^\circ$  ply. Warp yarns running parallel to the Y-axis are oriented at  $90^\circ$  with respect to the laminate and thus that ply would be a  $90^\circ$  ply. Warp yarns running at an angle  $\theta$  from the X-direction of the laminate are  $+\theta$  or  $-\theta$  plys (plus for the lowest angle in a clockwise direction from the x-axis, or minus for the lowest angle in a counterclockwise direction from the X-axis). Convention assigns the X-direction or  $0^\circ$  direction of the laminate in the direction of tensile or compressive loading. Assuming  $\theta = 45^\circ$  the stacking sequence for this laminate is  $[+45/0/-45/90/90/-45/0/+45]$  or in short hand:  $[+45/0/-45/90]_s$  where the 'S' subscript indicates symmetry.



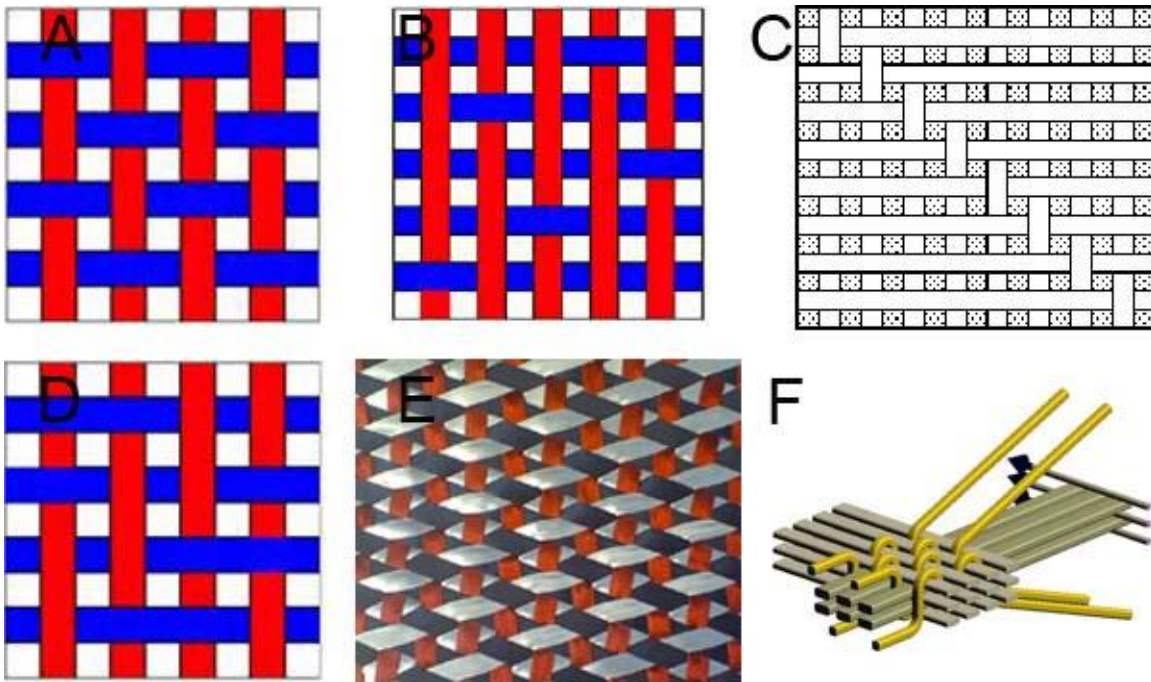


**Figure 1.13 Ply Orientation**

Perhaps most noticeable about a piece of fabric is its weave style. Different weave patterns exist so that a fabric can be made more or less pliable in a given direction, can provide more reinforcement along a certain direction, and creates a synergistic effect when multiple weave styles are used together in a single component. Figure 1.14 shows commonly used weave styles in composites manufacturing.

The plain weave is the oldest and most common weave (Figure 1.14A). The weave pattern of a plain weave is for the warp yarns to go over one weft yarn and under the next. Adjacent warp yarns follow the same pattern but in the opposite order: under one weft yarn then over one weft yarn. Basket weaves, a subset of plain weaves, have adjacent warp yarns going over and under the same weft yarns which gives the fabric the ability to shear slightly along the warp direction. Plain weaves have uniform strength in all directions and offer the least pliability due to the frequent interlocking of yarns. Satin weaves are often recognized by their shiny surface. Warp yarns float over several weft yarns and then tuck under one weft yarn before floating again, creating large flat surfaces that reflect light. Satin weaves are named for the number of weft yarns that are floated over, and consequently how many harnesses are needed on the weaving loom. Harnesses control which warp yarns are pulled up out of the way to insert a weft yarn; if a warp yarn is pulled up then it travels over that particular weft yarn. The number of harnesses needed is at least four and is one more than the number of weft yarns that are floated over. As shown in Figure 1.14B a 5 Harness Satin

weave therefore floats over four weft yarns at a time and is woven with five harnesses. As the number of weft yarns that are floated increases so does the strength and pliability of the fabric in the warp direction. Increased pliability is useful for laying up fabrics to fit to contoured surfaces, but if there is too much pliability than the fabric will shift disturbing the alignment of the yarns along a desired direction. For this reason satin weaves in excess of an 8 Harness Satin (Figure 1.14C) are rarely used.



**Figure 1.14 Weave Styles Used for Composites. A) Plain B) 5 Harness Satin C) 8 Harness Satin D) 2x2 Twill E) Triaxial Weave [14] F) Three Dimensional Weaving [15]**

Twill weaves are easily recognized by diagonal lines formed by adjacent floating yarns. The repeat pattern for a twill weave is over X and under Y yarns. The variable number of yarns that a warp yarn floats over in a twill weave is similar to a satin weave, but a twill weave can also vary the number of weft yarns that a warp yarn runs under. An example of a 2x2 twill is shown in Figure 1.14D. By changing the repeat pattern of a twill, the fabric's strength in the warp direction and its pliability are tailored.

Triaxial weaves have been introduced relatively recently in an effort to create a fabric that is strong in multiple directions. Applications where there are high shear forces have increasingly been using triaxial weaves to reduce the complexity of a layup using the more conventional plain, satin, and twill weaves. Figure 1.14E shows a  $-45^{\circ}/0^{\circ}/+45^{\circ}$  triaxial weave, where the red yarn is in the  $0^{\circ}$  direction, the white yarn in the  $+45^{\circ}$  and the black yarn in the  $-45^{\circ}$  direction. The  $\pm 45^{\circ}$  direction is popular since for a uniaxial tensile load the maximum resolved shear stress will be at  $45^{\circ}$  to this tensile load. Triaxial weaving can also use yarns that are more 'ribbon-like' (wide in 1 direction; narrow in the other) or more 'wire-like' (narrow in both directions, rigid) to be more or less similar to a traditional two directional woven fabric. Depending on the weave density, using ribbon-like yarns can save up to 50% or exceed by 50% the material weight needed to cover the same area as a two directional woven fabric. Having wire-like yarns uses about the same weight of material as a two direction woven fabric. Benefits of triaxial weaves also include high abrasion, tear, burst resistance, and high impact strength. The use of triaxial weaves around the spar cap of wind turbine blades is a growing trend. With a triaxial weave one might also mix yarn materials so that a higher strength heavier material can be used in the direction of greatest load, but lighter weight or cheaper material could be used in the less stressed directions.

Three dimensional weaves have interlocking yarns in the x-y plane as well as in the Z-direction. 3D weaves are also structurally superior to 2D weaves that are stitched together along the Z-axis. As shown in Figure 1.14F, 3D weaves leave yarns in the X-Y plane flat while creating an interlocked fabric by weaving yarns through the thickness (the Z-direction). 3D weaving started out in the lab in 1992 when Dr. Mansour Mohamed, a professor at NCSU's College of Textiles, filed what became US Patent 5,085,252 on the 3D weaving process. Dr. Mohamed started his own company, 3Tex, in 1994 when NCSU exclusively licensed Dr. Mohamed's patent to 3Tex. Eventually, many companies developed 3D weaving and 3D braiding technologies. 3D woven fabrics have superior fracture toughness, damage tolerance, and impact resistance, but are also more efficient in carrying load than an equal weight of 2D woven fabrics. Extremely important for composite laminate construction is interlocking in the Z-direction preventing delamination which is a common failure mode for layered materials under shear and to a lesser extent compression. A rather unique ability of

3D weaves is to create a sandwich construction where the foam core and fiber face sheets are fully integrated eliminating the need for adhesives [16]. Another use of 3D woven fabrics is to weave the fiber into a shape that is commonly used as a major structural component of design such as I-beams in aircraft.

## **1.5 Carbon Fiber Recycling Technologies and Methods**

Carbon fiber recycling has been studied for many years and several processes/technologies for recycling thermoset matrix composites have been demonstrated including: pyrolysis, fluidized bed, supercritical fluids, thermo-mechanical, and comminution. Pyrolysis has emerged as the most frequently chosen process for development of a commercial sized operation; however supercritical fluids are getting renewed interest by academics. Considering no single technology has resulted in a profitable business for recycled fibers from a wide range of feedstock, the ‘perfect’ solution is likely to incorporate multiple technologies, and thus an overview of the merits and demerits of each technology is warranted.

Pyrolysis by definition is the decomposition of organic material at elevated temperatures in the absence of oxygen. In practice pyrolysis is achieved using an inert gas environment (commonly nitrogen) or in vacuum. The equipment needed to build a pyrolysis oven/furnace is commonly available from other market sectors such as incineration, annealing of metals, and carbon fiber production. Fluidized bed recycling forces gas through a granular material to create a fluidized bed that offers excellent thermal conductivity and a higher thermal stability compared to a pyrolysis furnace. Solvent extraction processes require fewer moving parts, but require very expensive and exotic metals to withstand elevated temperatures, high pressure, and harsh solvents. Supercritical fluid reactors are straight forward to set up in a lab as a batch process, but maintaining the supercritical temperature and pressure over a large area has not been reported.

Several difficulties encountered with pyrolysis are control of temperature and oxygen content through the entire furnace. Heat and oxygen are released by decomposition of the organic polymer matrix. Optimal pyrolysis conditions are able to decompose the majority of

the polymer matrix without oxygen and then introduce a small amount of oxygen into the inert environment to clean the char residue off the fiber. The oxidation of carbon fiber is extremely sensitive to oxygen content and temperature. Often fibers are over oxidized, leaving pits in the fiber, or under oxidized, leaving chunks of burned resin on the fiber surface which is detrimental to fiber to resin adhesion. Desirable levels of oxygen have been reported to be 10% or less. Pyrolysis is suggested to be possible in a range of 200°C to 600°C, although more effectively in the range 300°C-500°C, and preferably, at least by the patent filed by Milled Carbon (West Midlands, UK), in the range of 425°C to 475°C [17]. Thick composites are difficult to handle because they will have a tendency to insulate the central region from the desired recycling temperature. At first the outer layers of a composite will heat up to the proper temperature, but in order for the central region to reach the correct temperature the tendency is to increase the temperature so that the core of the composite reaches the ideal temperature more quickly. Unfortunately, this burns the outer layers of the composite, and when the temperature of the furnace is reduced the inner region stays hot allowing over oxidation regardless of engineering controls to prevent this. A similar temperature control problem is found when pieces of composite of vastly different sizes are recycled; the time and temperature needed to properly recycle each piece is different so a mix of over, under, and properly oxidized fibers is produced. Carbon fibers recovered from a pyrolysis process have a 10-15% loss in strength and are delivered in a tangled arrangement unless special efforts are made to maintain fiber architecture [18].

The fluidized bed recycling process is classified as a thermal process, as is pyrolysis, but results in a more uniform heating of composite waste compared to a pyrolysis process. The bed material in a fluidized bed stores heat from the hot air blow in and the exotherming of waste material. Fluidization of the bed helps to more evenly heat and decompose the polymer matrix over the entire surface of composites. Like implemented at the University of Nottingham, a cyclone separator separates loose carbon fiber from unwanted materials like: lightning strike protection mesh, fasteners, and honeycomb, and breaks apart ply layers in a thick laminate (which allows the inner plies to be recycled without burning the outer plies). The downside to the fluidized bed process is that the fiber comes out as a tangled mess

resembling a bird's nest which is extremely difficult, if not impossible, to reuse in a composite fabrication process.

Supercritical fluids and hot solvent based recycling technologies have similar strengths and weaknesses. What's particularly appealing about these two technologies is the potential to achieve 100% strength retention in recycled fibers. Solvents and supercritical fluids are more forgiving than thermal processes: they handle a wide variety of composite materials systems, contamination (such as backing paper, metal, and nomex honeycomb), and sizes/ thicknesses of composites almost indiscriminately and with relative ease. Hot solvents have difficulty with thermoplastic materials whereas supercritical solvents are such strong solvents that thermoplastics and rubbers do not pose a challenge [19]. Hot solvent processes can be "slow" requiring several hours to work compared to supercritical fluids that do not need more than an hour depending on the fluid. Both hot solvent and fluidized bed carbon fiber recycling are batch processes and leave the fiber in a tangled mess like the fluidized bed. The most recent solvent based carbon recycling equipment was made by Adherent Technologies (*Albuquerque, NM*) and utilized a depolymerization catalyst. To handle rubber & thermoplastic toughened epoxy composites Adherent utilized a series combination of their solvent reactor and their "Phoenix" vacuum pyrolysis furnace. While this approach left clean and strong fibers the mass flow of the loose fiber through the pyrolysis furnace was severely reduced compared to feeding it composite material [20]. Even at the low mass throughput of Adherent's system it dwarfs any supercritical fluid reactors, which are still in lab scale development.

Comminution is the process of chopping, shredding, or otherwise size reducing material. The Japanese use an extreme case, milling waste composite to micron scale fiber length. D. Perrin et al. have developed a process where sheet molding compounds (SMCs) panels containing 20wt% fiber are cut into 5cm squares which are then dissolved in a buffered phosphoric acid solution, allowing for the separation of glass fiber, calcium carbonate filler, and polyester resin [21]. The fiber is then sorted to select the longest ones; average fiber length was increased from 2.5mm to 2-10mm. When the long fibers were reincorporated into thermoplastic matrices the loading also increased to 40wt%. This process has also been scaled up to deal with 200kg batches of waste SMC material [22]. J. Palmer et

al. have developed a process for replacing virgin glass fibers with fibrillar CF-Epoxy SMC recycle 5-10mm in length. SMCs made by replacing 20% by weight virgin glass fibers with CF recycle increased flexural modulus but decreased flexural strength and impact strength in comparison to a standard glass SMC. These results are attributed to poor adhesion between fiber and resin and a decrease in the fiber aspect ratio [23]. Since most carbon fiber recycling technology is geared towards thermoset matrices, a unique study to assess the feasibility of extrusion compounding comminuted thermoplastic composite with engineering thermoplastic resins has been undertaken by Dr. Kevin Gaw, a polymer engineer with Boeing Research and Technology.

### **1.5.1 Forms of Recycled Carbon Fiber**

Recycled Carbon fiber comes in a variety of forms based on the recycling process and on the intended application of the fibers. The most common forms are: milled, fabric, chopped, and entangled. Milled fibers are fibers that have been cut down or 'milled' down to very short lengths <1mm where the primary use of these fibers would be as filler to make a material more conductive or in an electro-magnetic interference shielding product. Fibers recovered from any recycling process can be milled or alternatively waste carbon fiber composite can be milled without going through a recycling process. Milled fibers have no practical use as a reinforcement material because their aspect ratio (length divided by diameter) is so small making load transfer from matrix to fiber impossible. Ideally carbon fiber composites collected for recycling are kept flat, sorted by fiber type, resin type, and weave style and if collecting prepreg waste, not fully cured. This extensive sorting and classification is a burden neither the waste generator nor the recycler wants to have, so often the level of organization is lacking. A milling process is insensitive to changes in fiber and resin type and is designed to break parts into miniscule pieces so the shape of the waste material doesn't matter either. As a filler product there is less emphasis on material composition or dialing in an exact mixture of properties. In general milling is an inexpensive recycling operation that produces cheap materials [24]. Carbon fiber recycling by milling has been prevalent in Japan for many years and in late 2010 "The World's First Commercial Scale Continuous Recycled Carbon Fibre Operation" operated by Recycled Carbon Fibre,

Ltd (RCFL) abandoned producing chopped fiber at lengths of 0.5in to 1.0in in favor of milling [25].

To integrate recycled carbon fiber into existing virgin fiber processing methods it is advantageous to either leave the RCF product as a woven fabric or to controllably chop the fiber into finite lengths often around 1in. lengths. Both pyrolysis and supercritical fluid processes can recover carbon fiber in a woven form. To date all supercritical fluid processes are lab scale so recovering fabric large enough to be reused is not possible. For recycling by pyrolysis the challenge in recovering a large piece of fabric is to uniformly heat and decompose the resin over a large area. To obtain chopped fibers a highly controllable feedstock needs to be available. Chopping of woven fabrics has been demonstrated by eMIT and RCFL has routinely used unidirectional prepreg tape as a feedstock for chopped recycled carbon fiber used in research projects. Chopped fiber can be used in any number of “short fiber” molding processes. Most demonstrator projects have used either injection molding or a slurry based molding process. Chopped virgin fibers are already used in injection molding, sheet molding, bulk molding, spray molding, and in slurry based processes to create fiber preforms for compression molding and/or resin transfer molding. Use of chopped recycled carbon fiber in these processes would be ideal: since at shorter lengths the strength of RCF is comparable to VCF, chopping VCF is an additional process that wastes the full potential reinforcement properties of VCF by reducing their aspect ratio, and there is a large demand for chopped fiber reinforced products.

Bundles of fiber can easily become entangled during fluidized bed processing, solvent recovery methods, and even with pyrolysis methods if the feedstock is not carefully selected so as to ensure fibers maintain their ordered arrangement such as in large sections of woven or unidirectional fabrics. Chopping waste composites into small pieces and then subjecting them to high velocity air causes recycled carbon fibers to knot up or penetrate into other layers of fibers creating a tangled mess similar to a bird’s nest. When fiber comes in this form it is unusable. Hand sorting or dispersing the fibers in a bath of water can untangle the fibers into a useable form.

To put short recycled carbon fibers into a more manageable form, they can be made into a “nonwoven” fiber preform. Nonwoven is a generic term for a form of textile material that



was not created by weaving, knitting, or braiding. Although referring to a material as a fabric implies the use of continuous material, nonwoven fabric is a frequently used term. Slurry based manufacturing processes, adapted from paper making, have been used to create a nonwoven product that is subsequently used in resin transfer molding or compression molding. Nonwoven fiber preforms do not have a clearly defined structure. Slurry based processes, such as the Wetlay, rely on binder additives and residual water for promoting cohesion between fibers. Other nonwoven processes are designed to create fiber interlocking in order for there to be cohesion. Nonwoven fiber preforms are characterized by the type of fiber(s) used, orientation and length of the fibers, porosity, areal weight, and thickness.

## **1.6 Composites**

The strict definition of a composite is the combination of two different materials. An expanded working definition would be the use of two materials, one serving as the reinforcing component and the other to bind the reinforcement together. This gives rise to the naming of the two components of a composite: reinforcement and matrix. The working definition implies a synergistic effect of mixing these two materials. Some ambiguity exists in the term “material”. The two “materials” of interest can range from being vastly different like rebar in cement or have the same atomic composition like graphite fibers in a carbon matrix, a so called carbon-carbon composite. In the case of a carbon-carbon composite the structure of the two carbon materials is different which is what makes each its own distinct material even if they are made out of the same elements. Functionally, the matrix phase of a composite transfers the load to the stronger reinforcement phase of the composite thereby supporting a minimal part of the load.

Since the reinforcement and matrix phase are designed to work together it brings up the interesting questions of: one, how well does the matrix transfer load to the reinforcement? and two, how does the composite behave if one of its two phases fails? The first question is measured in terms of the interfacial shear strength which tests how well the matrix phase sticks to the reinforcement stage. Chemical interactions and mechanical interlocking are the two factors that contribute to a material’s interfacial shear strength. For the second question there are two scenarios; either the reinforcement fails first, or the matrix fails first. If the

reinforcement fails first the stress on the composite is recalculated, taking into account that the load applied to the composite is now being applied to smaller area (because of the failure of the reinforcement stage). If this recalculated stress is higher than the strength of the matrix the composite fails. Importantly, there is a critical reinforcement fraction that must be reached for the reinforcement material to actually increase the strength of a composite over the strength of the matrix alone. Similarly, if the matrix fails first the stress on the composite is recalculated to see if the reinforcement phase can handle the stress. Also on a more practical note, the matrix would have to fail in such a way that the reinforcement phase was still bound together; otherwise the composite fails. The most common type of composite used in aerospace is the fiber reinforced plastic (FRP).

### **1.6.1 Processing & Molding Technologies**

To match the wide range of composite materials and products for which composites are used for there is a wide range of technologies to make the composite. Molding processes are geared towards specific industries so that an acceptable mix of composite properties, production rate, capital equipment cost, and operational costs are established to serve as a baseline expectation. For example injection molding produces products of minimal cost, has a high production rate, but molds are extremely expensive. In comparison, autoclave molding is slow, cure cycles are several hours long (often overnight), the autoclave itself is grossly expensive since it has to fit a large product volume, is pressurized around 10x atmospheric pressure, and must be able to control heating rates & temperature. The products produced by autoclave molding are of the highest quality and strength, and are naturally quite expensive.

#### ***1.6.1.A Compression Molding***

Compression molding is a broad term for applying mechanical pressure during curing and is used for a wide range of material forms. Two of the most widely used compression molding processes is matched die molding and press molding. In matched die molding the fabric is layed up on one half of the mold, and the other matching half, is used to apply pressure to the layup and may also be used to heat the layup. The mold halves are typically

made from high strength steel and are machined to the exact dimensions of the finished part. The cost of these molds is extremely high because they have to withstand very high pressures and because of the manufacturing cost associated with machining the mold. Prior to the composite being layed up the surfaces of the mold are coated with a mold release agent that keeps the composite from sticking to the metal faces of the mold. Matched die molding is commonly used in combination with hand layup, bulk molding compounds, and prepreg. Press molding uses the two flat platens of a mechanical press to apply pressure to a composite layup. The layup is constrained in a secondary container to keep dimensionality of the layup, to keep the layup from sticking to the mold, and to catch any resin that is squeezed out of the layup. Like matched die molding, the platens in press molding can be heated or cooled to control the processing temperature. The outer two inches of platen are considered a temperature transition region and should not be assumed to be at the process temperature. Therefore the size of the composite being molded should be smaller by at least four inches along the length and width of the platen. Press molding is an inexpensive method often used for research and prototypes. Compression molding processes consume large amounts of energy that is used to create the pressures and temperatures needed.

#### ***1.6.1.B Resin Transfer Molding***

Resin transfer molding (RTM) is used to transfer resin into fabric that will become the reinforcement phase of a composite. RTM is a process that injects resin into a closed mold containing the fiber reinforcement of a composite. The dimensions of the mold specify the dimensions of the composite panel. An injection system for RTM mixes resin and hardener (for 2 part systems) or mixes resin and catalyst (for a 1 part system) at a desired temperature to lower the resin viscosity. Vacuum is pulled on the exit outlet of the mold while resin is allowed to flow through and out of the mold removing any contaminants caught in the preform. The exit outlet is then closed and the RTM system pushes resin into the mold at a certain feed rate until a specified level of pressure is built up. As resin fills the mold cavity, it pushes back on the injection system creating the pressure that the injector feels. Once the desired pressure level is reached the injection system will administer more resin as needed to maintain constant pressure. As the resin cures it densifies, relieving

pressure. There are many variants of RTM and then variations on variants.

## **1.7 Key Players in Recycled Carbon Fiber “World”**

For better or for worse the Recycled Carbon Fiber Community is small where everybody knows everybody else, even if they do not play well together. Therefore it is worth describing the roles of the key players in the Recycled Carbon Fiber World to further appreciate the work presented in subsequent chapters as well as current and future literature. Starting with the businesses who have developed a carbon fiber recycling process there is: Adherent Technologies Inc. (ATI) (Albuquerque, NM), Recycled Carbon Fibre Ltd. (West Midlands, UK), Materials Innovations Technology (eMIT) (Fletcher, NC), and CFK Valley Stade (Hamburg, Germany). As two of the largest aircraft manufactures of commercial airliners Boeing and Airbus are closely following the status of carbon fiber recycling. The most active RCF research comes out of IMST/NCSU, University of Nottingham, and Imperial College London.

### **1.7.1 Boeing Research & Technology**

Boeing Research and Technology (BRT) has worked in partnership with the Commercial Airlines sector of Boeing to evaluate the properties recycled carbon fiber, evaluate the viability of various carbon fiber recycling operations, and develop products utilizing recycled carbon fiber. Additionally, BRT and Boeing Commercial Airlines develop working relationships with: researchers interested in recycled carbon fiber, companies who may manufacture RCF into an intermediate product, and composites fabrication companies who could use RCF in their product. Boeing has an interest in recycled carbon fiber so they can be a green company, reduce costs associated with disposing their carbon fiber composite waste, and using RCF has a cheap-light material to replace aluminum and glass fiber in loadbearing non-structural applications in their aircraft. As evident from presentations by Bill Carberry and Dr. Roland Thevenin and at The Global Outlook for Carbon Fiber 2010 conference Boeing's carbon fiber recycling approach differs from Airbus [26, 27]. In a different approach Boeing encourages CF recycling, works with various aircraft agencies and

companies involved with building and assembling aircraft, but does not try to incorporate CF recycling as part of their business operations. Boeing's way of pursuing CF recycling is through its participation in the Aircraft Fleet Recycling Agency (AFRA) and through BRT. BRT has used its funding to pay Universities such as University of Nottingham, Imperial College London, and NCSU to perform independent RCF testing.

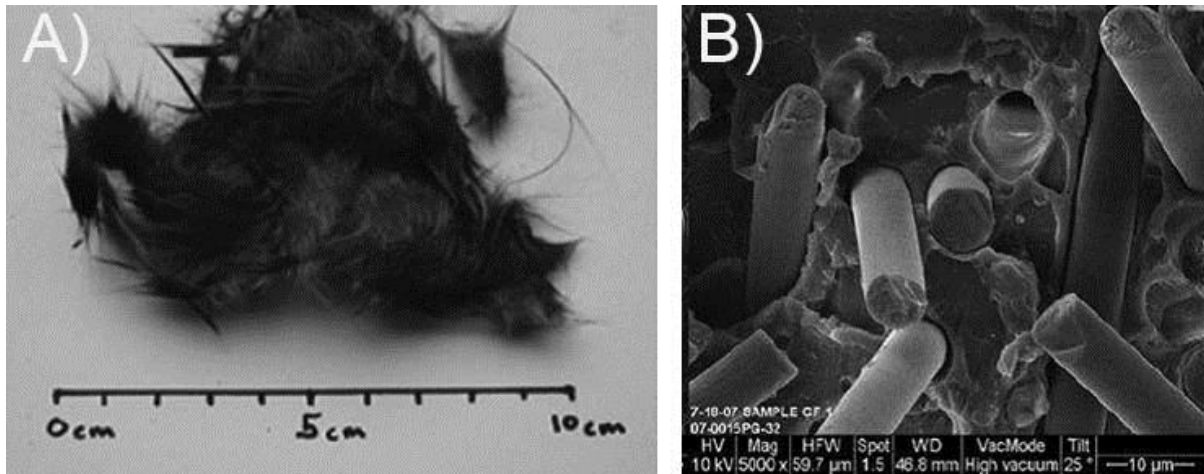
A typical RCF testing study works as follows:

1. BRT contacts multiple companies with CF recycling facilities and asks if they are interested in having their fibers tested
2. BRT will send the recycling companies waste carbon fiber composite with a known pedigree and then collects the carbon fiber recovered by the recycling process
3. BRT will then send these samples out for testing but generically labels the samples so the testing facility does not know who the fibers belong to.
4. Test results are reported back to BRT and the companies whose fiber was tested.

The testing facility may then apply their own labels to recycled carbon fibers so that when discussing test results BRT does not know who the fibers belong to (creating a double blind testing scenario). The single blind and double blind testing scenarios are used to keep BRT and the testing facility from jumping to conclusions and also build trust with the CF recycling companies that the tests are being conducted, thoroughly, and without bias. BRT can also be a liaison between universities experimenting with using RCF in composites and CF suppliers or composite manufactures such that materials can be donated for the research product or the university can rent time on the manufacture's equipment to conduct trial studies. Recently BRT announced at the Carbon Fibre Recycling and Reuse 2009 Conference that they had worked with Materials Innovations Technologies to demonstrate an armrest made from recycled carbon fiber [28]. Additionally, BRT has worked with NCSU to conduct a blending study using RCF to simulate sheet molding compounds (this effort is described in detail in chapter 5).

### **1.7.2 Adherent Technologies**

According to their website, ATI has been involved in Carbon Fiber Recycling since 1994, acquiring \$2.4million in government funding. ATI has demonstrated three processes for composites recycling: vacuum pyrolysis [20], low temperature thermal fluid [20], and high temperature thermal fluid [29]. Vacuum pyrolysis was chosen as an easy technology to implement and leaves no byproducts other than the carbon fiber. For common epoxy resins and for thin pieces of composite scrap this process produced recycled carbon fibers with favorable mechanical properties but with a layer of resin char that would prevent strong fiber to matrix adhesion [20]. A benefit of the pyrolysis process is its toleration of contaminants such as honeycomb, ash, wire, and plastic backing sheets. A previously explored alternative to vacuum pyrolysis is a high temperature (300°C), high pressure (500psi) thermal fluid system in combination with a proprietary catalyst [29]. Although this process was superior to vacuum pyrolysis giving 99.9% fiber purity and 90% strength retention in the fibers [29]; it was abandoned in favor of a thermal fluid system operating at a more manageable 150°C and 150psi. After the development of a new catalyst to operate at lower temperatures, the low temperature-low pressure system was able to recycle end of life composite scrap and recover fiber with 90% retention in tensile strength. However this process is not as tolerant of contamination and requires additional processing time for resins designed to operate at elevated temperatures [20]. Figure 1.15A shows the fiber form produced from ATI's low temperature-low pressure carbon fiber recycling process. The fibers are entangled making subsequent processing more difficult.

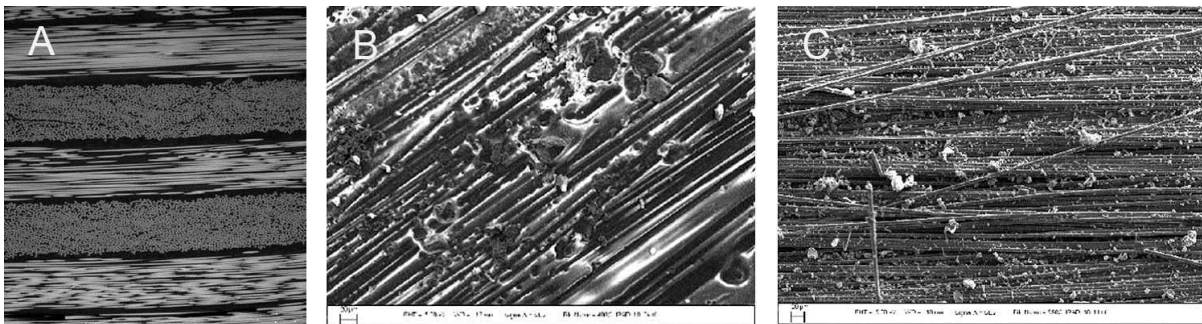


**Figure 1.15 A) Fiber recovered from end of life material using ATI's optimized low temperature-low pressure carbon fiber recycling process B) Fracture surface of ATI's recycled carbon fiber in a polycarbonate matrix**

The fiber strength results reported by ATI represent an optimized process in comparison to independent testing done at IMST/ NCSU around the same time [30, 31]. Connor et al [31] reported 60% strength retention of fibers from Adherent and no reduction in the elastic modulus. IMST/NCSU found for ATI's low temperature/low pressure process that the catalyst was not being removed from the fiber resulting in poor resin to fiber adhesion. Poor resin to fiber adhesion resulted in poor mechanical properties of injection molded polycarbonate composites using fiber recycled by ATI, compared to composites made from fiber recovered from Recycled Carbon Fiber's pilot process and a commercially available product RTP 385 [32]. Figure 1.15B shows significant fiber pullout and clean fibers confirming the low IFSS measurement.

In 2009 Adherent Technologies presented their efforts to recycle carbon fiber from State of the Art 2<sup>nd</sup> Generation Aircraft Composites such as those being used to build the Boeing 787 Dreamliner and the Airbus A350XWB aircrafts [19]. Using their established low temperature-low pressure process, capable of achieving 99% fiber purity for conventional epoxy resins, ATI found that 2<sup>nd</sup> Generation Aircraft composites have 20% unknown byproducts that were not dissolvable by their process. As seen in Figure 1.16A, the lines

running horizontally across the picture turned out to be toughening agents not part of the epoxy resin formulation. Thermogravimetric Analysis showed decomposition of the toughening agent at 600°C in nitrogen and 500°C in oxygen. ATI then tried their vacuum pyrolysis reactor, running at temperatures up to 550°C. At 400°C the toughening agent was not removed (Figure 1.16B). At 550°C most of the toughening agent was removed but substantial oxidation of the carbon fiber was occurring (Figure 1.16C). By pretreating the composite in the low temperature- low pressure recycling process followed by vacuum pyrolysis 99% fiber purity was achieved [19]. ATI has not reported any tensile strength measurements on these fibers, and is not actively pursuing commercialization of their processes for purposes of carbon fiber recycling. In 2009 at the first ever Carbon Fiber Recycling and Reuse Conference, organized by Intertech Pira in Hamburg, Germany, ATI did not report any additional work beyond what was presented at the 2009 SAMPE Conference in Longbeach, California [19, 33.



**Figure 1.16** A) Example of composite material used on Boeing 787 B) Vacuum Pyrolysis at 400°C C) Vacuum Pyrolysis at 550°C

### 1.7.3 Recycled Carbon Fibre, Ltd

Recycled Carbon Fibre, Ltd. (RCFL) is the carbon fiber recycling business arm of the Milled Carbon group. From 2003-2009 Milled Carbon developed and operated a pilot scale continuous pyrolysis process using a belt furnace. Upon completion of a new production scale carbon fiber recycling facility, a new company was formed under the Milled Carbon (MC) conglomerate, named Recycled Carbon Fibre. In 2005 IMST/ NCSU was able to test

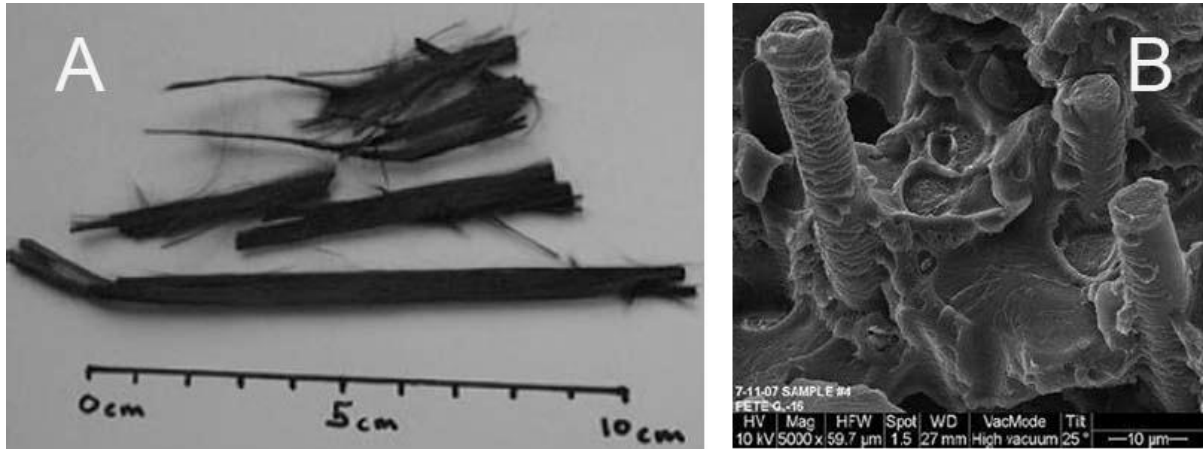


fibers from the Milled Carbon Pilot plant alongside fibers recovered from Adherent's wet chemical process [20]. MC fibers had 88% strength retention and 75% retention of elastic modulus. Based on feedback from IMST/NCSU Milled Carbon optimized their pyrolysis process.

In 2008 IMST/NCSU again conducted single blind testing of Carbon Fiber from potential recycling companies. After testing was complete IMST/NCSU learned fibers tested were from Milled Carbon and ENEA (Italian National Agency for new Technologies Energy and the Environment) /Karborek (a company based in Lecce, Italy that concentrates on technological innovation to bring high value products & processes to market). ENEA/Karborek brings the research and technological efforts into the partnership; while Karborek will be instrumental in building the recycling plant as well as making it commercially viable. The carbon fiber recycling facility operated by ENEA/ Karborek is located in close proximity to Alenia's Boeing 787 manufacturing facility to make waste collection as efficient as possible. ENEA/Karborek have presented at two SAMPE symposiums, most recently in 2009. In 2009 T800S uncured trim scrap was recycled using a lab scale pyrolysis process and a pilot scale process using a rotary drum furnace. ENEA/Karborek showed the manufacture of sheet molding compounds using these fibers had superior mechanical properties to glass reinforced SMCs used for structural needs in the automotive industry [34]. IMST/ NCSU conducted single filament characterization of the fibers recycled by ENEA/Karobrek the details of which are found in chapter 4. ENEA/Karborek have not announced future plans for their carbon fiber recycling process and have not discussed any further results at any international symposium.

Test results of MC's optimized pilot process were encouraging for standard modulus fibers: there was almost no loss in tensile strength at 10mm and 5mm gauge lengths, and elastic modulus retention was improved to be, at worst, 90% compared to virgin fibers [35]. In contrast, IM T800S fibers showed excellent strength retention at 6mm gauge lengths followed by rapid drop off in strength with increasing gauge length. Fibers at a 30mm gauge length showed a drop in strength of about 25%, which was still better than the unoptimized process, but fibers tested at a 60mm gauge length lost 34% of their strength compared to 28% for the unoptimized process. Standard modulus fibers also showed improved interfacial

adhesion over the optimized process as measured by the single fiber composite test [35]. Figure 1.17A shows a fracture surface on an injection molded tensile bar using AS4 fibers recycled using the optimized process (shown in Figure 1.17B); the high degree of resin to fiber adhesion is evident [32].



**Figure 1.17 A) Fiber from Milled Carbon/ Recycled Carbon, ltd optimized pilot scale pyrolysis carbon fiber recycling process B) Fracture Surface of fibers in A) incorporated into a polycarbonate matrix [32]**

Fibers recovered from the unoptimized process did not show as much sensitivity in strength to gauge length showing about 2% drop in strength for an increase in gauge length from 6mm to 30mm and then a 3% drop in strength from 30mm to 60mm compared to drops of 16% and 10% over the same gauge length intervals for the optimized process [35]. Cured trim scrap will have more resistance to high temperature oxidation than uncured trim scrap, while uncured trim scrap will partially cure as the pyrolysis process tries to decompose it. There are also a number of variables that can be optimized for one type or form of feedstock including temperature, temperature ramp rates, residence time and oxygen content; making recycling a variety of feedstock difficult when near virgin fiber properties are desired. Despite the loss in tensile strength of the T800S fibers recovered from Milled Carbon's optimized recycling process these fibers were still stronger than standard modulus virgin carbon fibers and their elastic modulus was higher than virgin T800S fibers at all gauge lengths.

In 2009 Milled Carbon announced the operation of the “The World’s First Commercial Scale Continuous Recycled Carbon Fibre Operation” and the establishment of a new company, Recycled Carbon Ltd, to manage the carbon fiber recycling efforts. The new facility boasts 60,000sq ft and a recycling capacity of 2.6 million lbs of CFRP waster/year. The furnace operates at 500°C-900°C and has dimensions of 100ft in length by 8ft wide [36]. To benchmark the new-larger pyrolysis furnace IMST/NCSU was asked by Boeing Research & Technology to conduct the fiber testing in a furnace position variability study. This study was designed to test the uniformity of the recycling furnace across its width. Samples of uncured T800S prepreg were sent down the left-hand side, center, and right-hand side of the recycling furnace, and additional samples were kept for 1-to-1 testing comparison purposes. The analysis is detailed in [37]. In summary there was significant variation in fiber properties from one side of the furnace to the other and tensile strength was severely degraded down to 30%-50% of the original strength. Surprisingly, there was also a decrease in elastic modulus by 10%-25%. RCFL optimized their pilot scale process based testing results on uncured trim scrap which produced fibers with minimal damage at 6mm gauge lengths. With both early efforts in their pilot scale process and commercial scale process RCFL has produced fibers with poor strength retention. Possibly as a coincidence the poorer testing results from RCFL has come from uncured trim scrap. RCFL has not been represented at any conferences since 2009 and also postponed their efforts to setup a recycling plant in the United States. Reports of process optimization by RCFL have been reported by researchers at Imperial College London [38, 39], but RCFL has also opted to exclusively sell milled fiber over fibers of longer length. Some of the process optimization work has shown how easily fibers can be oxidized with only a small increase in temperature, and the resulting fiber properties are on par with what IMST/NCSU found in 2010 [37].

#### **1.7.4 Materials Innovations Technologies**

Materials Innovations Technologies (eMIT) has a very successful fiber preforming process that is used to create a variety of three dimensional engineered preforms (3-DEP) for clients such as General Motors. The 3-DEP process has exceptional control over fiber

placement, including orientation, making thickness and weight variations minimal. 3-DEP has been demonstrated to work with glass, virgin carbon fiber (VCF), RCF, some natural fibers, and blends of the aforementioned fibers [363 Janney, Mark A. 2007;]. BRT introduced eMIT to recycled carbon fiber and after seeing how easily the 3-DEP process was able to process RCF, eMIT decided to develop their own CF recycling process, with some guidance from BRT. With the promising test results eMIT was able to attract investments into developing a large scale carbon fiber recycling facility. By establishing a CF recycling facility, eMIT could provide their own RCF raw material for their 3-DEP process.

In 2009 eMIT presented their efforts to produce recycled carbon fiber sheet molding compounds [40]. eMIT used their preliminary pyrolysis process to reclaim Toray T700 and T300 carbon fibers at 25mm lengths. Using a compression molding process 33% fiber volume and a density of  $1.3\text{g/cm}^3$  was achieved. Mechanical properties were evaluated by three point bend flexure tests. Flexure strength was 400MPa and flexure modulus was 23GPa.

Speculatively, in 2009 IMST/NCSU evaluated recycled SM T300 and T700G fibers from eMIT's preliminary pyrolysis process. These results were promising although IMST/NCSU has demonstrated through testing fibers from RCFL, that IM fibers can be more difficult to recycle and that scaling up your CF recycling capacity can result in large process variations [37]. eMIT's new CF recycling facility came online in late 2010 but is still working internally on optimizing the process. Considering short fiber composites are most popular for use in the automotive and ground transportation industries, and that short recycled carbon fibers have strength and stiffness closest to VCF, eMIT may already have a viable product for use in automotives. Even though having strong-short RCFs is good for cars it does not impress Boeing, and without BRT's stamp of approval eMIT's strategic location for their CF recycling operation next to Boeing's 787 assembly plant in Charleston, SC is irrelevant. As of January 2011, the two most viable Carbon Fiber Recyclers, eMIT and RCFL, have not shown a process that convinces BRT to recommend sending Boeing 787 Dreamliner manufacturing scrap to that recycler.

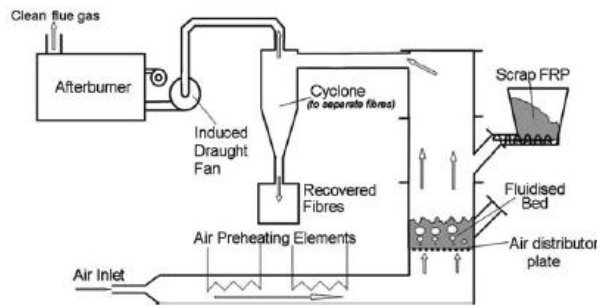
### **1.7.5 Aircraft Fleet Recycling Association (AFRA)**

Founded in 2005 to promote collaboration across the many industries that participate in aircraft manufacture, operation, and disposal; AFRA's main goals are to create best management practices for management of used aircraft parts and assemblies [41]. Starting with a core membership of 5 companies, the appreciation for AFRA has spread and now has 50 active members from 13 countries. Notable members include: eMIT, The Boeing Company, University of Nottingham, Milled Carbon Ltd., Pratt & Whitney, Huron Valley Fritz West, GE Capital Aviation Services, ATI, and Aircraft End-of-Life Solutions to name a few [42]. As part of their best practices AFRA is beginning to set standards for cataloguing of materials, maintenance procedures, and classification of waste. AFRA continues to be instrumental to the development of the carbon fiber recycling industry and the aircraft recycling industry in general.

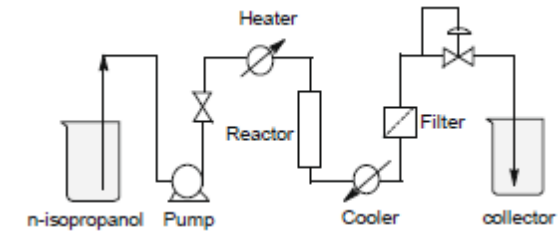
### **1.7.6 University of Nottingham**

The most substantial volume of academic work regarding recycled carbon fiber has come out of the University of Nottingham. Most of the work from University of Nottingham has been led by professors: Stephen Pickering, Nick Warrior, Koh Wong, Thomas Turner, G. Jiang, and L.T. Harper. With over a decade of work in the carbon fiber recycling The University of Nottingham has developed fluidized bed and supercritical fluid recycling processes, developed novel fiber preforms from recycled carbon fiber, has worked with Technical Fibre Products (TFP), in Cumbria, UK to manufacture nonwoven veils ranging from 20gsm to 200gsm in both random and oriented forms, and has studied resin flow through nonwoven fiber preforms as a function of tow filamentization and microstructural parameters. The fluidized bed process has been demonstrated as an alternative to pyrolysis processes, and to be particularly well suited for end-of-life waste (Figure 1.18). The fluidized process produces clean fibers with surfaces readily available for bonding, retains ~80% of fiber strength, and no measurable decrease in elastic modulus. Using cyclone separation to collect the recycled carbon fibers is particularly advantageous when dealing with highly contaminate feedstock, however the fibers are left in a fluffy form not suitable for immediate composites processing. Supercritical fluid recycling is of interest for its low

pollution and theoretical 100% detainment of original fiber properties. Supercritical n-propanol has been used at University of Nottingham (Figure 1.19) [43, 44], while supercritical water, carbon dioxide, ammonia, n-propanol and other alcohols have also been reported [45,46-49,50]



**Figure 1.18 Fluidised Bed Recycling at University of Nottingham [18]**



**Figure 1.19 Supercritical N-Propanol method for carbon fiber recycling [44]**

The University of Nottingham has conducted extensive work using a wetlay process to develop nonwoven fiber preforms for sheet molding applications (SMCs). To compare the mechanical behavior of one SMC to another it is useful to understand the properties of the fibers going into the SMC as well as the fiber architecture. Fiber architecture relates to how the fiber is arranged. For nonwoven mats, important parameters of fiber architecture are orientation of the fiber, the distribution of well filamentized fibers vs. fibers stuck together in tow like chunks, fiber length, and areal weight of the fabric. Additional information about the SMC construction like: fiber volume fraction, the molding process, molding pressure and final density of the SMC product is also invaluable when trying to explain differences in mechanical properties and failure mechanisms.

The cost of virgin carbon fiber SMCs exceeded conventional glass SMCs by a ratio of 20:1 while offering 80% of the weight and a little under three times the performance. This substantial price difference presents an opportunity for recycled carbon fiber based molding compounds targeted at two times the performance of glass SMCs and one-half to one-fourth the cost [51]. In 2006 a first pass was made with the intent of manufacturing a recycled carbon fiber molding compound. Grafil 34-700 carbon fibers were recycled using the

fluidized bed reactor yielding fibers with a tensile strength and modulus at the 15mm gauge length of 2.85GPa and 227.1GPa, respectively. Technical Fibre Products (TFP) turned the recycled carbon fibers into a nonwoven randomly oriented mat with a high degree of filamentization, a fiber length of 4.7mm, and an areal density of 100g/m<sup>2</sup>. To form the SMC, 20 layers of nonwoven fiber mats were stacked alternating with epoxy resin films before curing at 120°C for 30 minutes under 12.5MPa (~1800psi) applied by a hot press. The resulting SMC contained 40 volume percent fiber, had an ultimate tensile strength of 231.6MPa, an elastic modulus of 36.3GPa, and a density of 1.8g/cm<sup>3</sup> compared to a glass filled SMC with a volume fraction of 0.22, a tensile strength of 69.4MPa, and an elastic modulus of 9.2GPa [51]. While the recycled carbon fiber based SMC was clearly superior in strength there was still an interest in understanding the effect of binder concentration and type, reducing loft of the preform, and orienting the fibers to compare with anisotropic products.

In 2007 Wong [52] lead the efforts to make refinements to the molding process and study the level of pressure needed to obtain varying volume fractions of fiber. Toray T600 fibers were recycled using the fluidized bed process and converted into an oriented nonwoven fiber preform with an areal weight of 100g/m<sup>2</sup> by TFP. At a gauge length of 6mm, the RCFs had a tensile strength of 3.18GPa, and an elastic modulus of 218GPa which means these fibers were superior to those used in 2006. Fiber orientation was calculated by using second order tensor description of fiber elliptical shape parameters determined using optical microscopy. The fiber mats and resin sheets were layed up as before. This time the layup was vacuum bagged to allow for removal of air during compression and resin impregnation. Short fiber laminates (made with fibers ~8mm long) and long fiber laminates (fibers ~16mm in length) were manufactured at 20%, 30%, and 40% fiber volume by varying the molding pressure from 6.67MPa (~970 psi) to 13MPa (~1885psi). Maximum composite mechanical properties were a tensile strength of 314MPa and an elastic modulus of 37.1GPa for the short fiber laminate at 30 volume percent fiber. Fracture surfaces suggested strong interfacial adhesion. Compared to the SMCs made in 2006 there was a substantial increase in tensile strength, no significant improvement change in elastic modulus, and an improvement in density from 1.8g/cm<sup>3</sup> to 1.42g/cm<sup>3</sup>. Using oriented fiber mats explains the

increased tensile strength; however orientation of the fibers should also increase the stiffness. Thirty volume percent fiber loading resulted in the best mechanical properties for the short fiber laminates and the long fiber laminates, but the short fiber laminates were stronger and stiffer at all three fiber loading volumes than the long fiber laminates. For long fiber laminates a void content of 8% was found vs. 4% for short fiber laminates. Higher void contents in the long fiber laminate are explained by increased resistance to flow of the epoxy resin by longer fibers which is further explained by Harper et al. [53, 54]. The presence of voids is due to air trapped in the fiber mats and resin starvation.

A more recent investigation in 2009 [55] characterized sheet molding compounds made using Toray T300 fiber from RCFLs pilot scale pyrolysis process. We know the fibers were recovered from the pilot scale process since the single filament tensile testing results were similar to that found by IMST/NCU in 2009 [35], and there would not have been enough time for RCFL to optimize their commercial scale process beyond the results published by IMST/NCSU in 2010 [37]. At 6mm gauge length the recycled T300 fibers had a tensile strength of 4.16GPa and an elastic modulus of 217.8GPa. The increase in strength makes sense based on typical fiber strength loss during pyrolysis (<10% loss, strong gauge length dependent) compared to fluidized bed (~20% loss). TFP made the fiber preform according to the same process as in 2007, so 60% fiber alignment along with a high degree of filamentization is expected. Areal weight was measured to be 100g/m<sup>2</sup> and the weight average fiber length was determined to be 12mm. 200g/m<sup>2</sup> resin sheets were used as opposed to 300g/m<sup>2</sup> sheets used in 2006 and 2007. The reduction in resin sheet weight may have been in order to more uniformly distribute the resin. Additionally, a vacuum debulking procedure at room temperature was implemented before molding. 7MPa (1000psi) molding pressure was used to obtain SMCs with 30 volume percent fiber. Tensile strengths of 207MPa and an elastic modulus of 25GPa were reported for fiber loadings of 30 volume percent and void volumes of 5.5%. Fiber length distribution analysis showed only 30% of the fibers were longer than the critical length needed for load transfer from matrix to fiber, and all fibers were reduced to lengths of 2mm and shorter. The reduction in fiber length is due to the extreme molding pressures. Autoclave molding applies 0.7MPa (100psi) which is about 6-7 times atmospheric pressure; neither of which compare to the 7MPa (1000psi)



applied to increase fiber volume fraction. A relationship between resin flow and fiber length and fiber volume loading was observed. The lower the fiber loading the more interstitial space in the mat allowing for easier resin flow. However, the filamentized nature of the mat architecture results in a lower permeability. Further, the short fibers more easily fill up interstitial space. Decreased interstitial space and decreased permeability increase resistance to flow which increases void content. Fracture surfaces showed strong resin to fiber adhesion but since so few fibers were long enough to carry load, the overall composite mechanical properties were disappointing compared to University of Nottingham's earlier work in 2006 and 2007. Flexure strength was 318MPa and flexure modulus was 20GPa. Flexure properties were more similar to flexure properties reported by [40] when using T300/T700 RCFs in the 3-DEP process to make nonwoven preforms followed by compression molding at 1.7MPa.

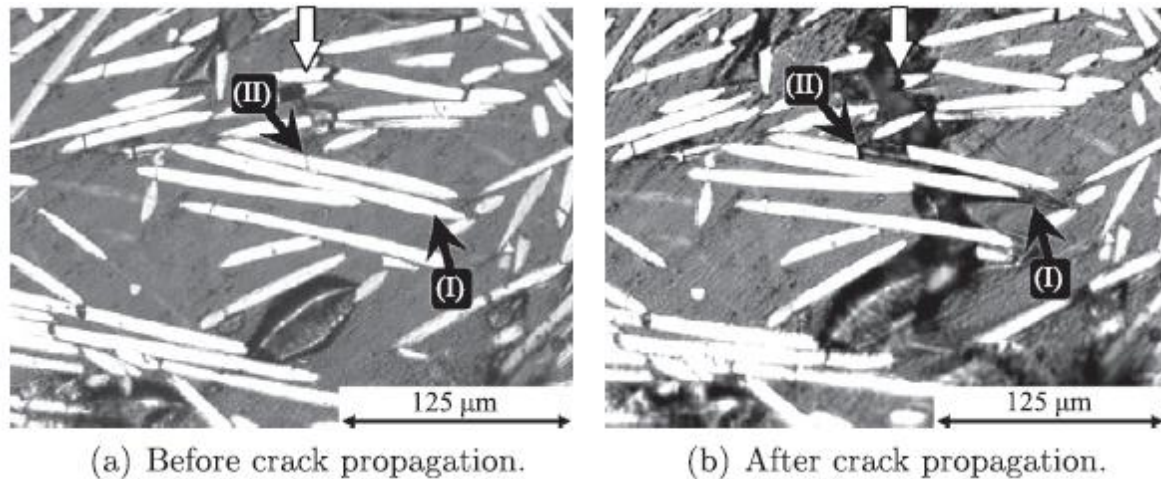
Chapter 5 of this thesis presents the combined efforts of IMST/NCSU to produce sheet molding compounds (SMC) using recycled carbon fiber. A similar paper making nonwoven mat process was used to make the fiber preforms, however the mats are only slightly oriented as a result of the flow of water along the machine direction. In contrast to the University of Nottingham's process, resin transfer molding was used to mold the nonwoven fiber preform, creating hydrostatic pressure that we believe prevented substantial reduction in fiber lengths. Also, based on our analysis in [37] we believe the fibers received from RCFL for IMST/NCSU's SMC study are significantly weaker than those used in The University of Nottingham's SMC work. As will be shown in more detail IMST/NCSU's SMC have a lower fiber content, weaker fibers, are manufactured using resin transfer molding, but have similar mechanical properties to the SMCs made by University of Nottingham.

### **1.7.7 Imperial College London**

Imperial College London began investigations of using recycled carbon fiber in 2009. Imperial College London (ICL) focuses on mechanical modeling including failure mode analysis. ICL has recently collaborated with the University of Nottingham to conduct another recycled carbon fiber sheet molding study. University of Nottingham manufactured

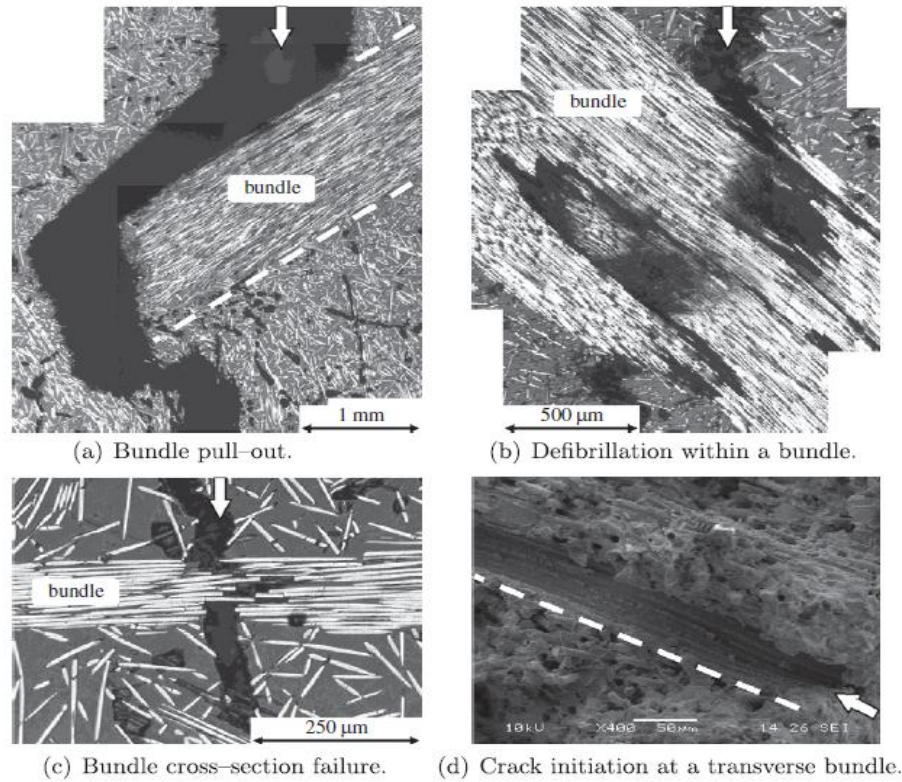
the SMC from the same fibers and using the same compression molding process as they reported on in 2009. ICL carried out single fiber pull out tests to measure fiber to matrix adhesion and showed the recycled carbon fibers have just as strong if not slightly stronger resin to fiber bond than virgin fibers. As would be expected the tensile strength and modulus of the SMC are nearly identical to that reported by University of Nottingham. Constituent analysis revealed 27% fiber volume, and 7% void volume. The most valuable portion of this study was characterizing the failure modes under tension and compression.

Under tension the test specimens failed in a brittle manor; cracking across the face of the specimen and through its thickness. Microscopically the crack either followed the fiber matrix interface or a path through fibers broken by the molding process (Figure 1.20) [56]. Examination of fracture surfaces of Micro Compact-Tension ( $\mu$ T) specimens showed two distinct morphologies. Rougher surfaces and longer fiber pull out lengths correlated with stable crack propagation behavior recorded during the compact-tension (CT) testing. Smoother surfaces and shorter pull out lengths corresponded to unstable crack propagation and crack jumping. In the transition region between stable crack propagation and unstable crack propagation the reinforcement architecture was found to be in the form of bundles (undispersed tow chunks).



**Figure 1.20 Crack propagation in RCF-SMC under tension. “Failure mechanisms under stable tensile crack propagation (specimen loaded; wider white arrows represent the macroscopic crack-direction): through (I) fibre–matrix interface and (II) previously-fractured fibres.” [56].**

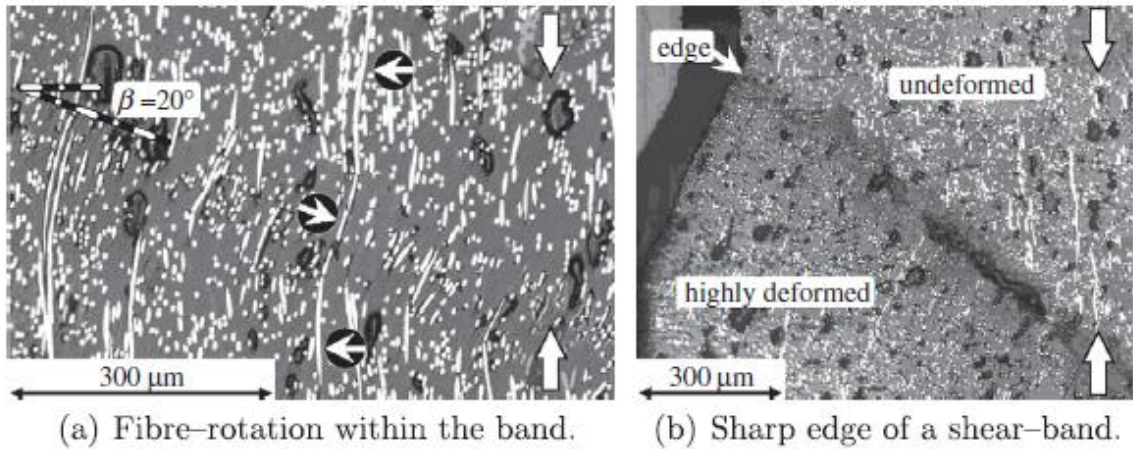
Reinforcement architecture is again found to drive the failure mechanism when considering the failure of the fiber bundles not dispersed into filaments by the wetlay process. In [57] these bundles were found to act as a toughening agent, deflecting cracks. Additionally, these bundles are more resistant to breaking under pressure than dispersed filaments [58]. Prior to this analysis the school of thought was to 100% disperse and filamentize the RCF when making a nonwoven preform in order to achieve the highest levels of uniformity possible. In [56] Pimenta et al. observe thick fiber bundles will fail by pulling out completely or by separating into individual filaments (Figure 1.21a,b). Thin bundles are not as effective at absorbing crack propagation energy; they simply fracture across their width. Thin bundles oriented traverse to the longitudinal direction of the composite and thus more parallel to crack propagation act as stress concentrators favoring initiation and propagation of cracks along their fiber to matrix interface (Figure 1.21c,d).



**Figure 1.21 "Failure Mechanisms of fibre-bundles under tension (wider white arrows represent the macroscopic crack-direction)" [56]**

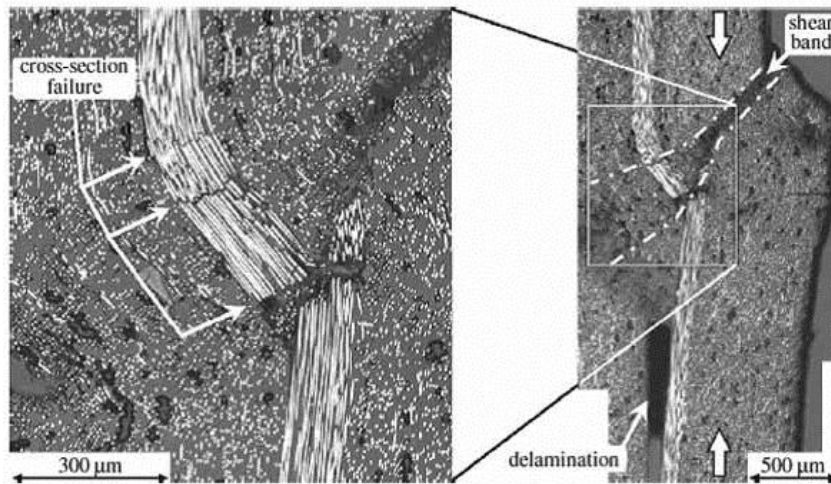
Failure under compressive loading was similarly characterized with Compact Compression (CC) testing to calculate compressive  $G_{Ic}$  fracture toughness and  $\mu C$  specimens were used to examine microstructural response and failure to compressive loads. Compressive failure behavior shares characteristics of fiber kinking and traverse compressive failure of unidirectional composites. Fiber kinking is identified by the rotation of fibers in shear bands. As reported in similar literature studying fiber kinking in fiber reinforced composites: the bands initiate at low angles ( $\beta \sim 20^\circ$ ) (Figure 1.22a), the band angle increases with increasing load, and sometimes the shear band broadens and sharp edges are defined (Figure 1.22b) [59]. Traverse unidirectional failure shown in Figure 1.22b is represented by the majority of shear bands evolving into sharp shear bands ( $\beta \sim 54^\circ$ ), with no visible plastic deformation [56, 60]. Matrix yielding is a fundamental process in both fiber kinking and traverse compressive failure in unidirectional composites, but a simple matrix yielding model

does not account for the low shear band angles ( $\beta \sim 20^\circ$  and  $\beta \sim 45^\circ$ ) observed at early stages of deformation.



**Figure 1.22** Microstructural features during compressive loading [56]

Simple uniaxial tension and compression tests show the SMC is stronger and more ductile in compression than in tension. Microstructurally, the formation of shear bands during compressive loading is a much better energy absorber than crack propagation seen under tensile loading, consistent with a larger  $G_{Ic}$  in compression than in tension. As seen in Figure 1.23, thick tow bundles aligned with the compressive load are subject to cross section failures and delamination which absorb energy over a wide loading range, contributing to increased toughness [41, 58]. Future work may include further development of the model presented in [57] to include prediction of additional material properties or for different composite architecture. Additionally, an effort with RCFL to optimize furnace temperature has been shown in [38, 39] and may yield ongoing work, studying the effect of different types of feedstock.



**Figure 1.23 Compressive Failure of Recycled Carbon Fiber SMC**

## 1.8 Barriers to Commercialization of Recycled Carbon Fiber

Even with the development of composite aircraft that are 50% by weight composite and half of that weight also being available in the form of trim scrap there is not a market for



recycled carbon fiber despite 5-10 years worth of research showing the applications for recycled carbon fibers.

### **1.8.1 Why Recycle?**

The desire for high performance materials to meet aggressive design requirements in the wind energy, aviation, and defense industries fuels an ever increasing demand for carbon fiber. With more carbon fiber comes more carbon fiber waste in many forms including: expired prepreg, manufacturing excess, and trim scrap. Companies that generate carbon fiber waste have a desire to be environmentally friendly by not landfilling their waste. Carbon fiber recycling reduces the amount of landfilled waste and reclaims the carbon fiber as raw material. Regulations or the desire to be environmentally conscious encourages companies to consider recycling carbon fiber composite as opposed to incineration or landfilling. European legislation (Directive 2000/53/EC) regulating disposal of vehicles has mandated that by 2015 a maximum of 5% by weight of the vehicle can be landfilled, 85% must be recycled or reused, and the remaining 10% may be subject to energy recovery.

([http://ec.europa.eu/environment/waste/elv\\_index.htm](http://ec.europa.eu/environment/waste/elv_index.htm))

Although there are no regulations surrounding composite disposal in the United States, companies in the aerospace and automotive sectors are still making an effort to be more sustainable. The Boeing Company has announced very specific milestones for recycling 787 Dreamliner manufacturing waste: all composites manufacturing scrap from the Fredrickson, Wa & Charleston, SC sites are to be recycled by the 4<sup>th</sup> quarter of 2011, and in 2016 many interior components are to be recycled (ex. glass reinforced polymer composites and carpets) [26]. The tensile strength of recycled carbon fiber (RCF) is greater than or equal to glass fiber and the stiffness of RCF is comparable to virgin carbon fiber (VCF) [35]. From a materials design standpoint RCF can be used to supplement heavier, costlier, or harder to obtain materials. Substantial work still needs to be done to show RCF can be integrated into existing composite fabrication processes without a loss in performance. Having the ability to use RCF, as a supplementary material poses a potential cost savings opportunity when conventional materials are in short supply or become more expensive. It takes 90,000kJ - 270,000kJ to make a pound of virgin carbon fiber and 4,680kJ – 16,200kJ to recover a pound

of recycled carbon fiber; so the energy savings of recycling compared to producing VCF offers a cost savings opportunity [61].

### **1.8.2 Limited motivation to recycle**

For carbon fiber recycling to take off as an industry there must be motivation from waste generators to want to recycle carbon fiber scrap and there must be the willingness for someone else to run a carbon fiber recycling business. Motivations to recycle are: wanting to be labeled as green, to reduce waste disposal costs, to get paid for recyclable material, to avoid or to comply with environmental legislation, and a want to be environmentally responsible. As mentioned earlier there is a trend in European Legislation to reduce the amount of landfilled mass, but no such legislation, or prospect of, exists in the United States. Without a legislative motivation, the motivation needs to be the allure of a profit from participating in carbon fiber recycling. The biggest obstacle to identifying a profitable way to participate in recycling is the logistics of transporting scrap from the generator to the recycler.

#### ***1.8.2.A Logistics and Cost Sharing of Transporting Scrap from the Generator to Recycler***

One part of the logistics battle is getting the waste generator and recycler to agree on what forms of waste are mutually beneficial. An excellent way of representing this was presented at the Global Outlook for Carbon Fiber 2010 [62] (Figure 1.24). The key to operating a profitable carbon fiber recycling business is to produce high value recycle. Recycled fibers filled with contamination, tangled knots of carbon fiber, and milled fibers are worthless for any composites molding application. The time and energy needed to clean up the fiber supply outweighs the cost benefit of using recycled carbon fiber. Contamination such as wire and honeycomb ash may be unavoidable when processing end of life scrap, but a recycling process such as the fluidized bed or vacuum pyrolysis are tolerant of these materials and are designed to separate them from the valuable carbon fiber. In order for a recycler to be interested in recycling contaminated carbon fiber composites waste, it better be free. On the other hand neatly sorted scrap, flat sheets of prepreg, or woven trimmings are excellent materials to use for injection molding or a recycled carbon fiber woven laminate.



These types of products actually retain the high strength & stiffness and low density that makes using virgin carbon fiber so attractive; therefore the recycler will be able to sell these materials at a high cost.

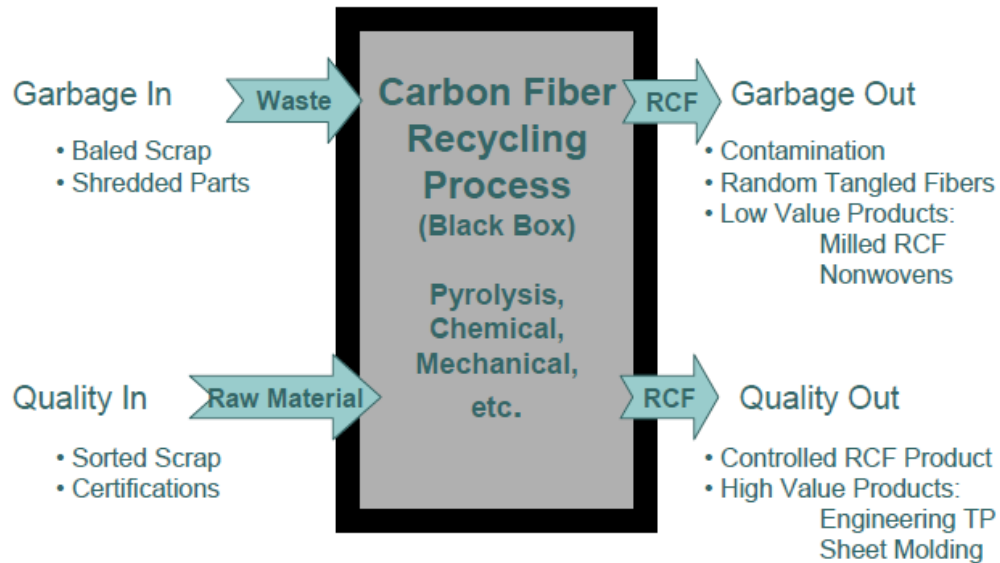


Figure 1.24 Importance of understanding limitations and strengths of the recycling process [62]

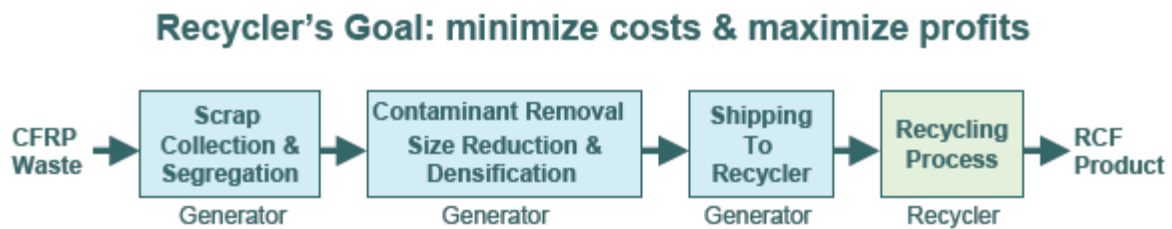


Figure 1.25 Waste Generator Model. The scrap generator profits, while the recycler takes a hit giving an overall value of zero. [62]

Once the waste generator and recycler agree on what types of materials make sense to recycle they must agree on how to share the cost of recycling. Hunter [62] has proposed three models of cost sharing: scrap generator, recycler, and cooperative. In the waste generator model they are only concerned with having a green image and will not participate in preparing the scrap for recycling. In this model carbon fiber waste is pretty much discarded like trash and left for the recycler to collect, organize, and transport. Since there is

very low control over the quality and type of scrap available for collection; the recycler cannot certify the properties of the recycled carbon fiber except to certify them as low, yielding little profit.

In the recycler model (Figure 1.26): the waste generator bears the burden of collecting, organizing, and transporting the scrap leaving the recycler to focus on the nuts and bolts of recovering carbon fibers from polymer resins. A recycler wants a long term waste supply contract including certification and classification of the incoming materials. Of course the waste generator and recycler certify and classify their materials differently so ultimately both lose money.



**Figure 1.26 Recycler Model.** It is the generator's reasonability alone to prepare the waste for the recycler. [62]

In the cooperative model (Figure 1.27) the waste generator can honestly say they are a “Green” company while the recycler is able to sell the recycled carbon fiber at a high price allowing them to pass on some profit to the waste generator. In a cooperative model the recycler has representation onsite at the waste generator's facility. This can range from being in the form of a single person to guide and train the employees at waste generator's facility to the other extreme where employees of the recycler can be onsite to take over the responsibilities of collection, certification, and classification. The geographical positioning of carbon fiber recyclers in the vicinity of large carbon fiber waste generators suggests the desire to cooperate. Materials Innovations Technologies has set up in South Carolina to be next to Boeing's 787 assembly plant in Charleston, and will also be in a prime position to receive scrap from Spirit Aerosystems when they move their manufacturing from Wichita, Ka to Kinston, NC. As indicated by their website, Spirit Aerosystems has contracts with

Boeing and Airbus for manufacturing components of their next generation aircraft that extensively use composites [63].

### Generator/Recycler Cooperation: shared cost and maximum profits for both



**Figure 1.27 Cooperative Model.** Both waste generator and recycler bear the burden of preparing the scrap but both are able to profit since the carbon fiber recovered is highly valuable.[62]

### 1.8.3 The Need for Recycled Carbon Fiber Products to Fit into Existing Applications & Manufacturing Processes Used for High Strength Materials

As of yet there is not an active market for a recycler to simply sell their recycled carbon fiber in part because so few people know how to use recycled carbon fiber. Recycled carbon fiber in general is difficult to work, and knowing what processes work well with what types of carbon fiber will be invaluable. Composites that are of high value often come from injection molding [32, 64] and sheet molding compounds [23, 55, 56,40], intermediate value composites can come from bulk molding compounds [65] or resin transfer molding, and low value uses of carbon fiber are electromagnetic interference shielding, lighting strike protection mesh, thin veils for use as membranes, as conductive filler, and filler in thermoplastic composites [22, 23, 66,67]. All of these applications have been demonstrated, but it is important to continually make improvements to the process and to make comparisons to existing products. Additionally, developing equivalency certifications for using alternative types of fiber reinforcement such as blended recycled and virgin materials need to be developed for the carbon fiber recycling industry to begin its integration into the composites world. The use of blended materials or all recycled materials creates a more steady raw material supply chain and different portions of this supply chain can be selected for different cost and performance levels. An excellent summary of which fiber forms can be used in which processing route and the resulting type of material you can get has been prepared by

Dr. Steve Pickering, as part of the Global Outlook for Carbon Fibre conference in 2010, and is presented below in Figure 1.28 [68].

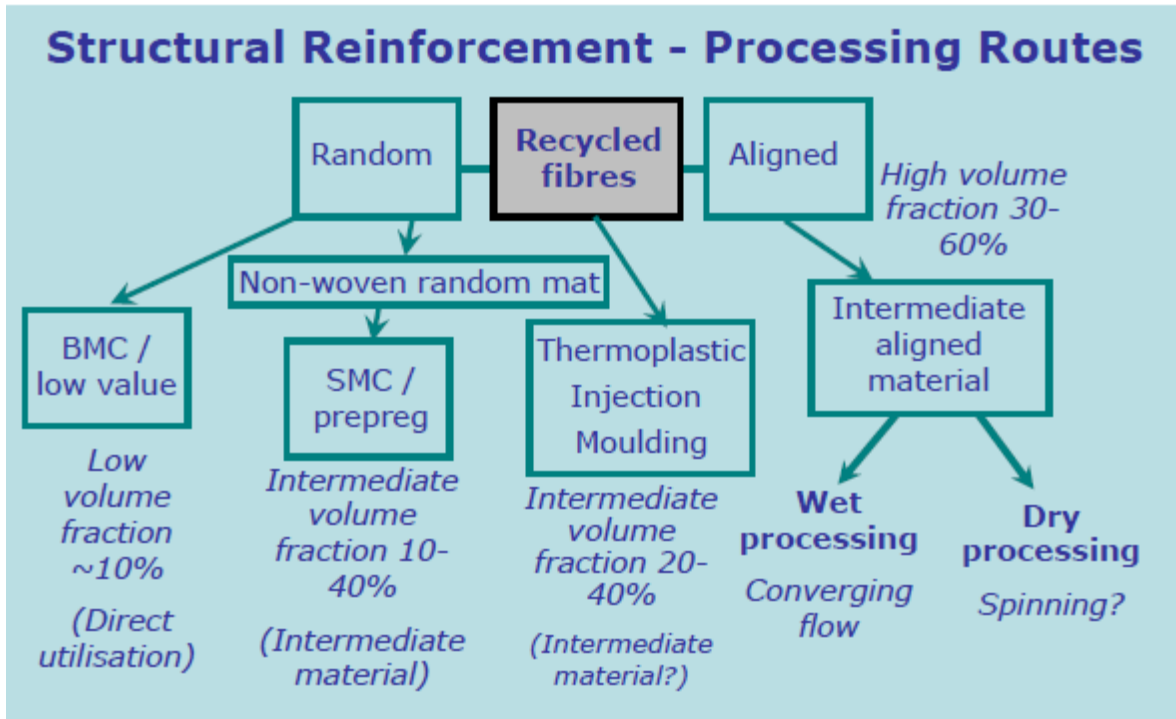


Figure 1.28 Fiber form, processing, product relationships [68]

## **2. Organization of Work To Be Presented In the Following Chapters**

This thesis details the characterization of many different recycled carbon fibers over a period of three years. Three questions this research seeks to address are:

1. What is the effect of the recycling process and scrap material on recycled carbon fiber properties?
2. What are the mechanical properties of recycled carbon fiber compared to virgin carbon fiber?
3. What is the performance of recycled carbon fiber composites and what processing considerations need to be made in order to incorporate recycled carbon fiber into composites.

This research was conducted in collaboration with multiple industrial partners. Thus the materials studies were a mix of the most conveniently available and most valuable to these partners so a design of experiments that analyzed each type of scrap material from each recycling process could not be conducted. For example T300 fibers were recycled by Milled Carbon from cured and uncured trim scrap, but only T800S fibers recycled by Milled Carbon from uncured trim scrap were available. Also Materials Innovation Technologies did not have any recycled T800S fibers available for testing to compare the effect of recycling processes on T800S fibers recycled from uncured trim scrap. Additionally, the processes used to recycle the carbon fibers in this work are proprietary and confidential so IMST/NCSU has no knowledge of the process conditions. Therefore, correlations made between test data and processing conditions are an informed and responsible analysis but not absolute fact.

The next two chapters of this thesis show analysis of recycled carbon fiber on the single filament level. The analysis in both these chapters is the same but different scrap material and recycling processes are considered. The third and final analysis chapter (Chapter 5) discusses processing steps needed to incorporate recycled carbon fiber into a composite and how this differs with respect to virgin carbon fiber. Chapter 5 also presents

mechanical testing data of composites made from 100% virgin carbon fiber, 100% recycled carbon fiber, and a 50/50 recycled/ virgin blend of carbon fibers.

## **2.1 Background Information**

The following three chapters discuss characterization of recycled carbon fibers and the use of these fibers to make a sheet molding compound. Chapter 3 details characterization of recycled carbon fibers (RCF) from Milled Carbon's and ENEA/ Karborek's pilot scale carbon fiber recycling facilities. Both of these processes used are a form of pyrolysis. These test results are also compared to previously published test results [30, 31]. Chapter 4 discusses the properties of RCF recovered from RCFL's commercial recycling facility, fibers from eMIT's batch pyrolysis process, and two other fibers from an undisclosed source. Challenges of scaling up recycling capacity are discussed based on the variable fiber quality found from testing fibers from RCFL. Additionally, test results show trends in recycling carbon fiber are presented. These trends include increased difficulty in recycling IM fibers, strong gauge length dependence of fiber strength retention for pyrolysis processes, superiority of RCFs derived from aerospace materials compared to carbon fibers used in consumer goods, and RCF's retention in elastic modulus. Some discussion is also given to explaining test results based on the type of material recycled, i.e. end of life, uncured trim scrap, and cured trim scrap. Chapter 5 presents the combined efforts of Boeing Research and Technology to produce a sheet molding compound using fibers recovered from a production scale facility, namely RCFL. These fibers are manufactured into nonwoven mats using the wetlay process. Discussion on mat uniformity and manufacturing method are conducted to highlight differences between this wetlay process and the wetlay process used by Technical Fibre Products to produce mats for The University of Nottingham. The resin transfer molding process is also described to show how it differs from the compression molding method used by University of Nottingham and Materials Innovations Technology. Mechanical test results are presented that show how performance changes based on the type and mix of fibers used in the nonwoven fiber preform. Results from ASTM reinforced plastics mechanical testing standards are compared against results from Boeing internal test

methods. Finally, the mechanical performance of the SMCs under tension and flexure are compared against relevant literature. Taken together these three chapters represent the evolution of carbon fiber recycling from pilot scale to initial production and culminating in the use of RCF recovered from a production facility to make a carbon fiber reinforced composite product that is used by the automotive and aerospace industry.

### **3. A Comparison of Chemical, Morphological, and Mechanical Properties of Various Recycled Carbon Fibers**

Joseph P. Heil, Michael J. Hall, Davis R. Litzenberger, Raphael Clearfield, Jerome J. Cuomo  
North Carolina State University  
911 Partners Way  
Raleigh, NC 27695-7907

Pete E. George, William L. Carberry  
The Boeing Company  
9725 East Marginal Way  
Seattle, Wa 98108

*Manuscript to be submitted to the Journal of Advanced Materials*



### **3.1 Abstract**

Carbon fiber reinforced polymer composites (CFRPs) are highly desired materials exhibiting superior strength to weight properties. The main drawback to CFRPs is their high cost. The value of carbon fiber, along with the volume of manufacturing excess and end of life material, make recycling of carbon fiber an economically viable prospect in addition to an environmental responsibility. Over the course of the past three years NCSU has evaluated the chemical, morphological and mechanical properties of various recycled carbon fibers. Standard and intermediate modulus carbon fibers from multiple pyrolysis based carbon fiber recycling companies were tested to examine the influence of fiber type, material feed form, and recycling process on the properties of recycled carbon fibers. Electron microscopy was used to evaluate surface morphology and fiber diameter. X-ray Photoelectron Spectroscopy was used to evaluate surface chemistry. Finally, single filament tensile tests and resin embedded fiber fragmentation tests were used to evaluate strength, stiffness and apparent resin to fiber interfacial shear strength. Recycled fiber in general performed well in comparison with virgin fiber with some apparent trends in performance for standard vs. intermediate modulus fibers. Stiffness and adhesion performance was close to that of virgin fiber with strength performance retention at 70 to 100% of virgin fiber mostly dependent upon fiber type. Consistency of performance will be a critical factor for recycled carbon fiber to gain acceptance especially in making progress towards higher performance applications.

### **3.2 Introduction**

The lifecycle cost advantages of carbon fiber epoxy composite materials have made them the new material of choice for commercial airframe structural components. Carbon fiber composites enable lighter weight structures, reducing fuel burn per passenger mile. Carbon fiber components are less susceptible to corrosion and fatigue than aluminum, reducing maintenance costs and enabling better cabin environmental conditions. The Boeing 787 Dreamliner, well into production and scheduled for first flight in 2009, consists of greater than 50% by weight carbon fiber reinforced epoxy composite. The Airbus A350 XWB,

entering the detail design phase and scheduled for 2013 delivery, also uses greater than 50% by weight carbon fiber reinforced epoxy. Between them, Boeing and Airbus have orders for over 1500 aircraft which will have wings, fuselage and empennage components made mostly of carbon fiber reinforced materials. This poses a new set of challenges however for manufacturing excess and end of life structure material disposal. Viable processes for recovering valuable carbon fiber from these materials are poised to enter production scale offering recycling options for both factory excess and end of life carbon fiber (EOL) composite materials. Understanding the quality of the fiber produced from these processes will enable their use in the highest value applications providing greater economic incentive for recycling. In 2006 Boeing and The Institute for Maintenance Science Technology at North Carolina State University (IMST/NCSU) began work to evaluate recycled fiber from end of life F18 carbon fiber composite stabilators with promising results [30, 31]. Since then our work has shifted focus to uncured and cured factory excess materials used in the 787 production process. Various samples of these materials were provided by Boeing to two recyclers for reclamation. Boeing then provided the recovered fibers to IMST/NCSU for a double blind evaluation where the recovery source of the fiber was not known by IMST/NCSU and the results when presented back to Boeing, by IMST/NCSU, were not linked to the recycler source. Other fibers used in Boeing production from the Fredrickson, and Washington Composites Manufacturing Center sites were also evaluated.

**Table 3.1 Overview of fibers evaluated**

<b>Fiber Code</b>	<b>Fiber Type</b>	<b>Source</b>	<b>Recycler/ Process</b>	<b>Year Tested</b>
<b>V-AS4</b>	AS4	Hexcel Virgin Fiber	N/A	2006
<b>CF1</b>	AS4	End of Life Part*	Adherent Technologies	2006
<b>CF1-L</b>	AS4	End of Life Part*	Adherent - longer fibers	2007
<b>A-MC-EOL</b>	AS4	End of Life Part*	Milled Carbon	2006
<b>A-MC-EOL-O</b>	AS4	End of Life Part*	Milled Carbon optimized	2007
<b>VT300</b>	T300H	Cytec Virgin Fiber	N/A	2007
<b>T3-MC-CTS**</b>	T300H	Cured Trim Scrap	Milled Carbon	2008
<b>T3-MC-UTS</b>	T300H	Uncured Fabric	Milled Carbon	2008
<b>V-T700G</b>	T700G	Toray Virgin Fiber	N/A	2007
<b>RCF2</b>	T700G	Uncured Fabric	Milled Carbon	2007
<b>V-T800S</b>	T800S	Toray Virgin Fiber	N/A	2007
<b>T8-MC-CTS</b>	T800S	Uncured Scrap	Milled Carbon	2008
<b>T8-EKL-CTS</b>	T800S	Cured Trim Scrap	ENEA/ Karborek Lab Scale	2008
<b>T8-EKP-CTS</b>	T800S	Cured Trim Scrap	ENEA/ Karborek Pilot Scale	2008
<b>T8-MC-CTS</b>	T800S	Cured Trim Scrap	Milled Carbon	2008
<b>VIM7</b>	IM7	Hexcel Virgin Fiber	N/A	2006
<b>I-MC-CTS</b>	IM7	Cured BMI Trim	Milled Carbon	2008

\* End of life F18 Stabilator

### 3.3 Experimental Procedure

IMST/NCSU's standard characterization procedure includes Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), single fiber tensile tests, and the single fiber composite test (SFC). Table 3.2 below shows the information gained from each test.

**Table 3.2 Summary of characterization techniques.**

<b>Technique</b>	<b>Information Determined</b>
SEM Scanning Electron Microscopy	Fiber diameter, contamination Surface texture, defects
EDS Energy Dispersive Spectroscopy	Elemental composition of bulk
XPS X-Ray Photoelectron Spectroscopy	Atomic Percent, %'s of Carbon Bonding
Tensile Test 3 gauge lengths	Fiber Tensile Properties, Weibull Shape & Scale Parameters
SFC Single Fiber Composite Test	Critical Fragment Length, Resin to Fiber Adhesion

### **3.3.1 Scanning Electron Microscopy (SEM)**

A Hitachi S-3200 variable pressure SEM was used to capture low magnification images from 900-6,000X for fibers studied in 2005-2007. This particular microscope helped give an overall perspective of the fiber set. To gain a more detailed image of the fibers, a JEOL 6400F field emission SEM was used to obtain high magnification/resolution images. In 2008 all fiber images were taken with the JEOL 6400F.

#### **3.3.1.A Energy Dispersive Spectroscopy (EDS)**

An Oxford Isis EDS system was used in conjunction with the variable pressure SEM (Hitachi S-3200). By bombarding the carbon fibers with an electron beam and collecting the x-rays, relative elemental presence was determined. Fibers studied in 2008 were examined using this EDS system even though no images were taken for morphological analysis.

### **3.3.2 X-ray Photoelectron Spectroscopy (XPS)**

A Riber XPS was used for fibers studied in 2005-2007 utilized while a Kratos Analytical Axis Ultra XPS with a spot size of 300 $\mu$ m x 700 $\mu$ m was used for fibers studied in 2008. Both instruments utilized Monochromated Al K- $\alpha$  radiation and Kasa XPS software. A complete scan was conducted on each carbon fiber sample, and the elemental peaks were identified along with their atomic percents. In addition, by using an XPS data deconvolution technique for the C1s carbon peak, the types and relative amounts of carbon bonding present on the carbon fiber surface was determined. This information is important for estimating the potential bonding and interfacial adhesion of the recycled carbon fibers with polymer matrices.

### **3.3.3 Single Fiber Tensile Testing**

Single fiber tensile testing was done at the Cornell University Department of Fiber Science under the supervision of Dr. Anil Netravali. The fiber diameter was measured using an optical microscope and filar ocular lens. Tensile tests were performed on an Instron Universal tester (Model 5566). All tests were run at 0.4/minute strain rate. Fibers were tested at three different gauge lengths during each testing session. Fiber gauge length ranges were not held consistent between test sessions. Single filament test values were derived from test populations using weibull statistics as single filament strength is a function of flaw frequency.

### **3.3.4 Interfacial Shear Strength**

The single fiber composite (SFC) test was conducted at Cornell University by Dr. Anil Netravali. The SFC test is a well-established method to determine interfacial shear stress. In this technique, a single fiber is embedded in a resin material that has a fracture strain at least 3 times than that of the fiber. The SFC specimen is strained at a constant rate at which point the fiber breaks at multiple points where the fiber fracture stress has been reached. As the fiber breaks into shorter fragments, the shear force that is transferred along the fiber interface cannot build up a high enough tensile stress to break the fiber further. At this point, no

further fragmentation occurs and the final fragment length can be measured to obtain the critical length for the interfacial shear stress calculation [69].

### **3.4 Results & Discussion**

#### **3.4.1 Scanning Electron Microscopy**

Images used for fiber diameter measurements were taken using a JEOL 6400F Field Emission SEM. These images were then processed using Revolution software from 4pi Analysis, Inc. The photos were loaded using the software, and the “Measure” tool in Revolution was used to make diameter measurements (Table 3.3). As virgin and recycled fiber were not from the same lots manufacturing variability may have contributed to the differences in fiber diameter. Also some morphologies such as that of the T800H can present different diameters depending on the viewing angle. These factors may help explain why some of the measured recycled fiber diameters are more than virgin fiber diameters. In general there were no drastic losses to fiber diameter. The largest fiber diameter reduction for a smooth fiber was from VCF1 to T8-EK(L)-CT for Torray T800s, an 8% change.

**Table 3.3 Fiber diameter measurements.**

Fiber Type		Fiber Code	Average	StDev
Intermediate Modulus		VIM7	4.92	0.280
	Hexcel IM7	I-MC-CTS	4.71	0.246
		VT800S	5.36	0.176
	Toray T800s	T8-MC-UTS	5.28	0.184
	24k Tow	T8-EK(L)-CT	4.92	0.111
		T8-EK(P)-CT	5.36	0.097
		T8-MC-CTS	5.20	0.158
Standard Modulus	Toray T700G	VCF2	6.60	0.166
	12k Tow	RCF2	6.35	0.179
		VT300	7.23	0.245
	Cytec T300	T3-MC-UTS	7.52	0.317
	3k Tow	T3-MC-CTS*	7.68	0.572
	Hexcel AS4	VAS4	7.07	0.370
		CF1-L	7.47	0.260
	A-MC-EOL	7.55	0.220	

### 3.4.2 Scanning Electron Microscopy - Fiber Appearance

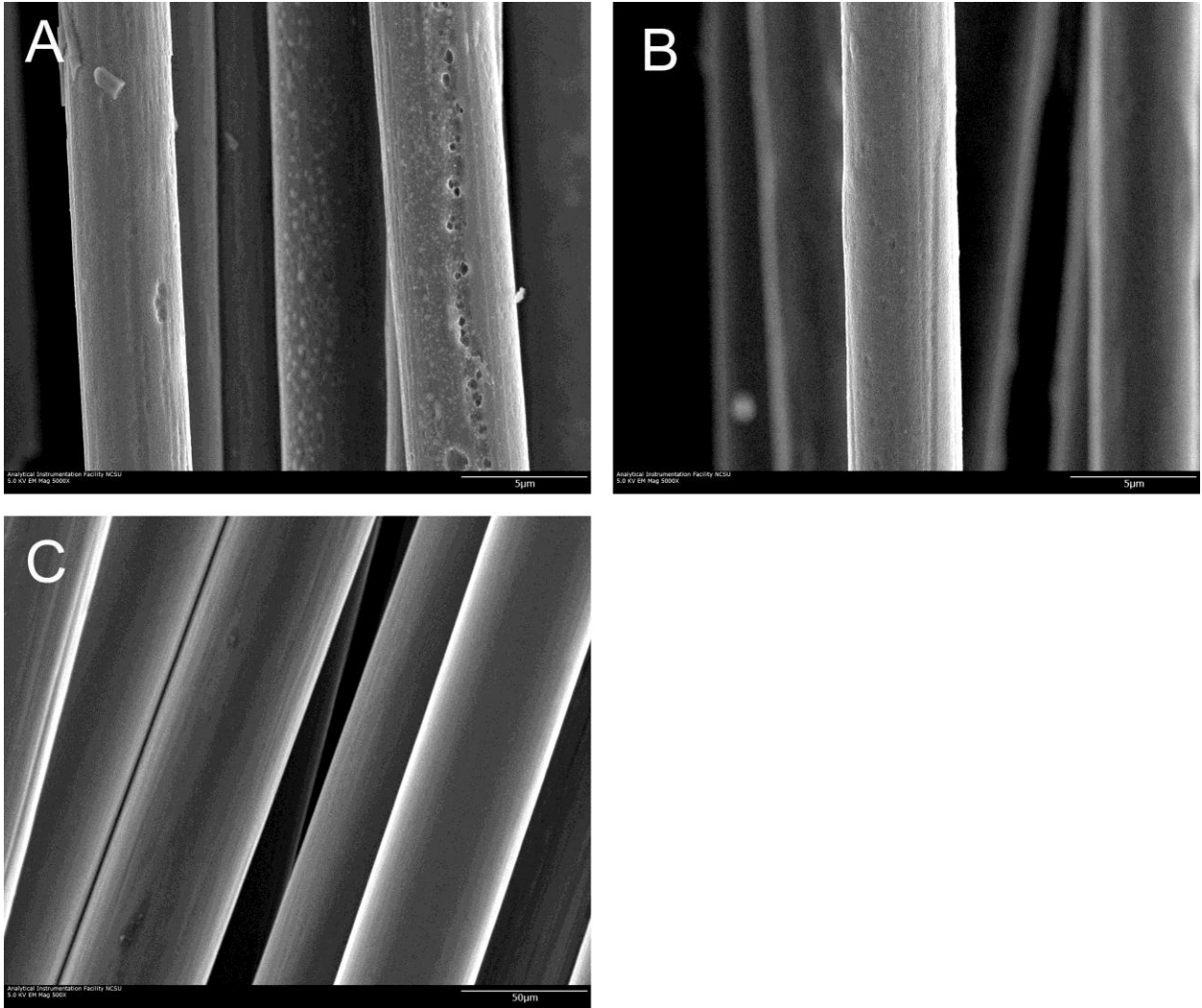
Fiber appearance before and after reclamation was evaluated with emphasis on changes in fiber surface morphology and apparent residue or contamination. Differences in apparent surface damage levels were noticed between reclaimed Standard Modulus class fibers (30-35 Msi) and Intermediate Modulus class fibers (40-44Msi). Intermediate Modulus fibers recovered with pyrolysis based processes showed signs of surface pitting. Various levels of residue and/or contamination were seen in all recycled fibers and in one instance on virgin fiber. Virgin and recycled Hexcel IM7 and Toray T800S intermediate modulus fiber samples were characterized. IM7 fiber was reclaimed from cured Cytec 5250-4 BMI material while

the T800S fibers were reclaimed from uncured and cured Toray T3900-2 epoxy materials. All fibers were recycled using pyrolysis processes from various recyclers as shown in Table 3.1.

#### **3.4.2.A     *Hexcel IM7 Intermediate Modulus Fiber***

Figure 3.1 shows recycled and virgin IM7 fibers. Figure 3.1c was taken in 2006, while Figure 3.1a and Figure 3.1b were taken in 2008 after upgrades resulting in different imaging conditions. Figure 1a and b., I-MC-CTS recycled fiber, show what would appear to be damage in the form of pitting. The particulate on the surface of the virgin fiber sample (Figure 3.1c) is not representative of the quality of virgin fiber and may be external contamination. While the image quality is not as good for the virgin fiber no pitting is visible. Figure 3.1c shows fibers with less evidence of fiber damage. Random sampling of three representative areas of the I-MC-CTS fiber showed various levels of pitting from mild to severe. Figure 3.1a. also shows what might be char residue on the fiber in the left hand side of the image, a spotted appearance to one fiber in the background, and a fiber in the right hand side of the image whose surface appears to curve inwards towards a line of pits in the fiber center. Again, an important question to ask is if the pitting is in the carbon fiber itself or in an incompletely removed resin char layer on the surface of the fiber. Depth profiling with Energy Dispersive Spectroscopy (EDS) and mass spectrometry are among the characterization methods being pursued to definitively identify residual resin char or contamination vs. fiber surfaces. Figure 3.1b also shows a striation that is groove-like in appearance, a feature not present in the virgin fiber image.

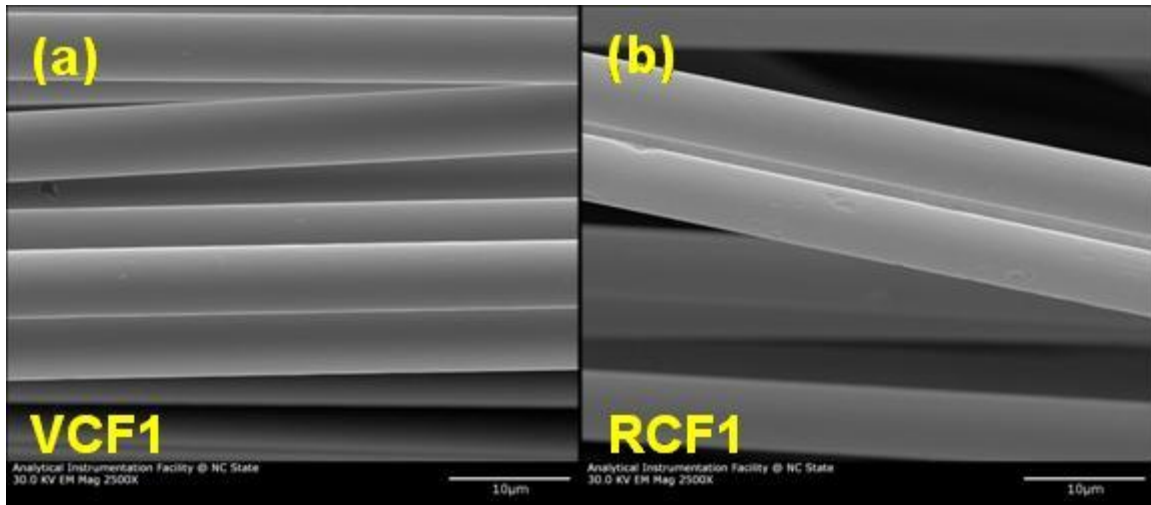




**Figure 3.1** A) I-MC-CTS Hexcel IM7 with heavy pitting. B) I-MC-CTS Hexcel IM7 with less visible pitting. C) Virgin Hexcel IM7

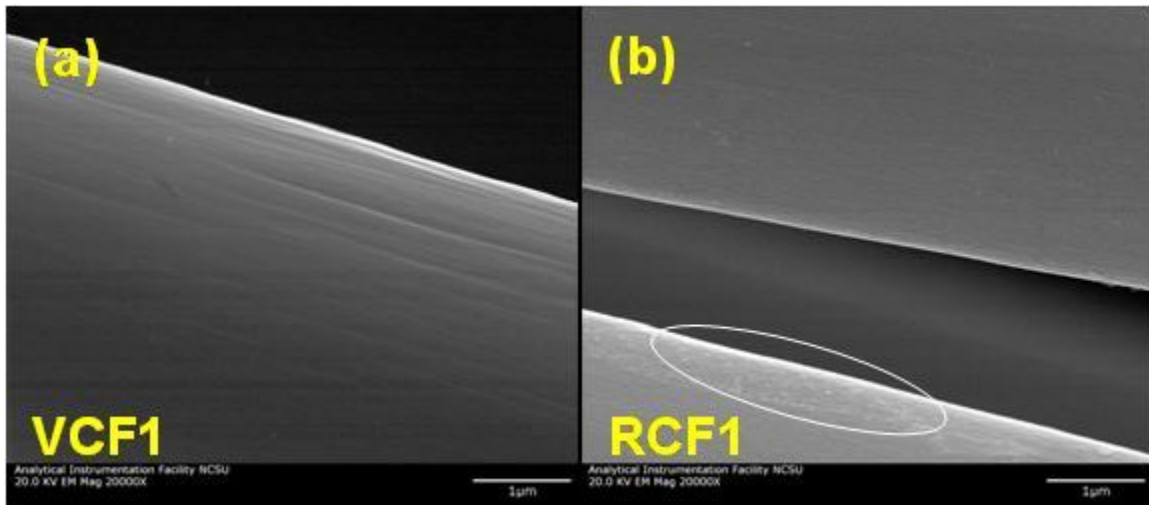
#### **3.4.2.B      *Toray T800S Intermediate Modulus Fiber***

Fiber recycled from uncured unidirectional trim scrap was designated T8-MC-UTS. In 2008, three fiber samples T8-EK(L)-CT-7 were derived from BMS spec 8-276 cured trim scrap; each sample was recycled using a distinct process as listed.



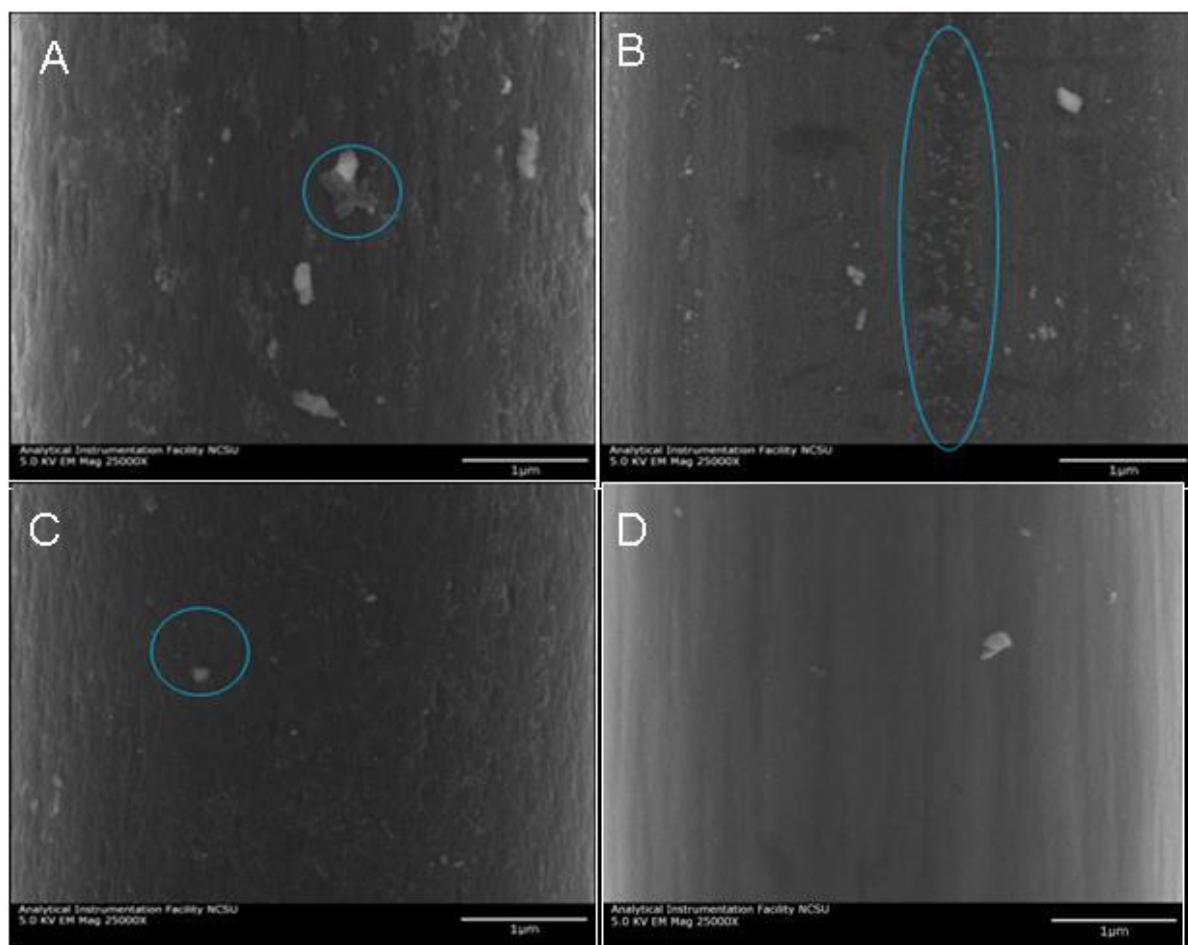
**Figure 3.2 Variable pressure SEM micrographs of T800S fibers. A) Virgin fiber B) Fiber was recycled from uncured prepreg using pyrolysis and shows evidence of pitting.**

Figure 3.2a is a micrograph of a virgin T800s, used as a control fiber, showing clean and smooth surfaces. It can be seen from Figure 3.3b that the recycled fiber, T8-MC-UTS, has some form of pitting on its. However, this type of behavior was not seen in other locations and looked much less damaging than the pitting observed in the T800s fibers. There also seems to be some sort of residue or surface texture present on the surface of T8-MC-UTS in Figure 3.3b which was also seen on RCF2 and fibers recycled in 2007.



**Figure 3.3** Field emission SEM micrographs for fiber sets VT800S (a) and Milled Carbon T8-MC-UTS (b). VT800S shows striations on the surface. T8-MC-UTS shows a residual surface material

Figure 3.4 shows high magnification images used to reveal more detailed surface differences. The control fiber is distinctly cleaner and has a smooth surface. The large particles in the control image are not bound to the fiber and are most likely handling contamination and therefore not representative of the fiber quality. Figure 3.4A reveals recycled fibers that have a spotted appearance where Figure 3.4B shows recycled fibers that have particles sitting on the fibers. Milled Carbon’s recycling process leaves the fibers clean (Figure 3.4C), but with a texture different from that of the control as seen in Figure 3.4D.



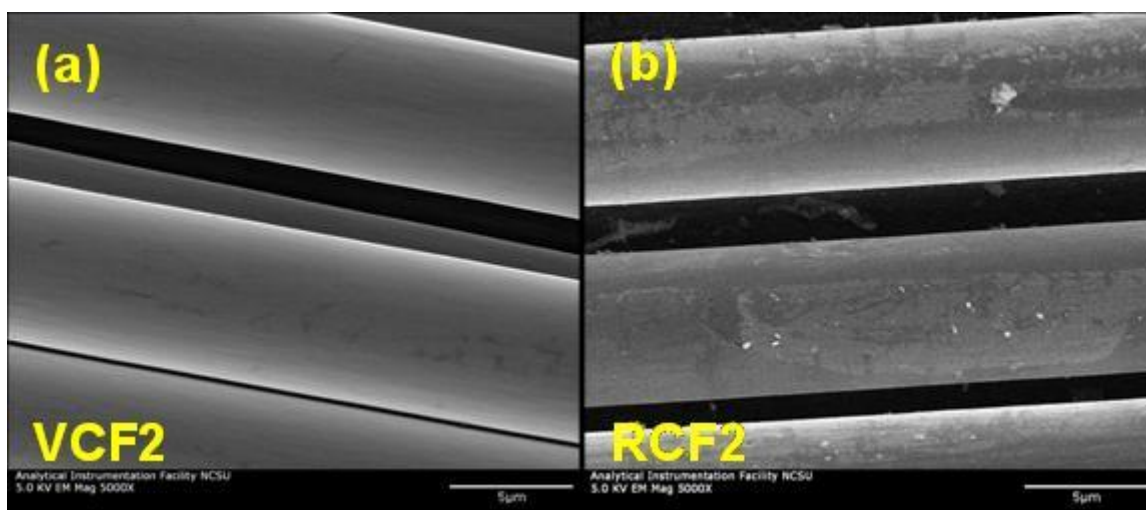
**Figure 3.4 A) T8-EK(L)-CT with particulate tightly bound to surface. B) T8-EK(P)-CT with evidence of residue on surface. C) T8-MC-CTS with loosely bound particulate D) Control virgin fiber with clean striated surface.**

T8-EK(L)-CT is deeply textured which contributes to an increase in surface roughness (a). The particulates are sufficiently bonded to the T8-EK(L)-CT fiber to resist strong electrostatic forces that try to lift the particulate off the surface of the fiber. T8-EK(P)-CT seems to have a residual surface coating on the fiber (Figure 3.4B). Most of the fiber looks cloudy while the circled area does not have a cloudy appearance. Unlike the fibers shown in Figure 3.4A and Figure 3.4B, the particulates on T8-MC-CTS (Figure 3.4B) recycled by Milled Carbon Ltd. were seen to partially lift off the surface of the fiber due to electrostatic forces. A degree of surface roughness more than that of T8-EK(L)-CT but less than that of

T8-EK(P)-CT is also evident on T8-MC-CTS. T8-EK(L)-CT and T8-MC-CTS show evidence of surface oxidation. Figure 3.4D shows the original morphology of these fibers showing striations and a slightly ribbed or rippled appearance.

#### **3.4.2.C      *Toray T700G Standard Modulus Fiber 12k Tow***

Whitish surface material is visible and well defined when observed under the field emission SEM in Figure 3.5b for pyrolysis recycled T700G similar to that observed in other recycled fibers. There also are some particulates present on the surface of these fibers. The virgin fiber (Figure 3.5a) exhibits a dark mottling. This type of appearance was seen throughout all images and observed areas of this sample.



**Figure 3.5 A) Virgin Toray T700G fiber. B) T7-MC-UTS recycled fiber from uncured prepreg with a non-uniform surface coating and some surface particulates.**

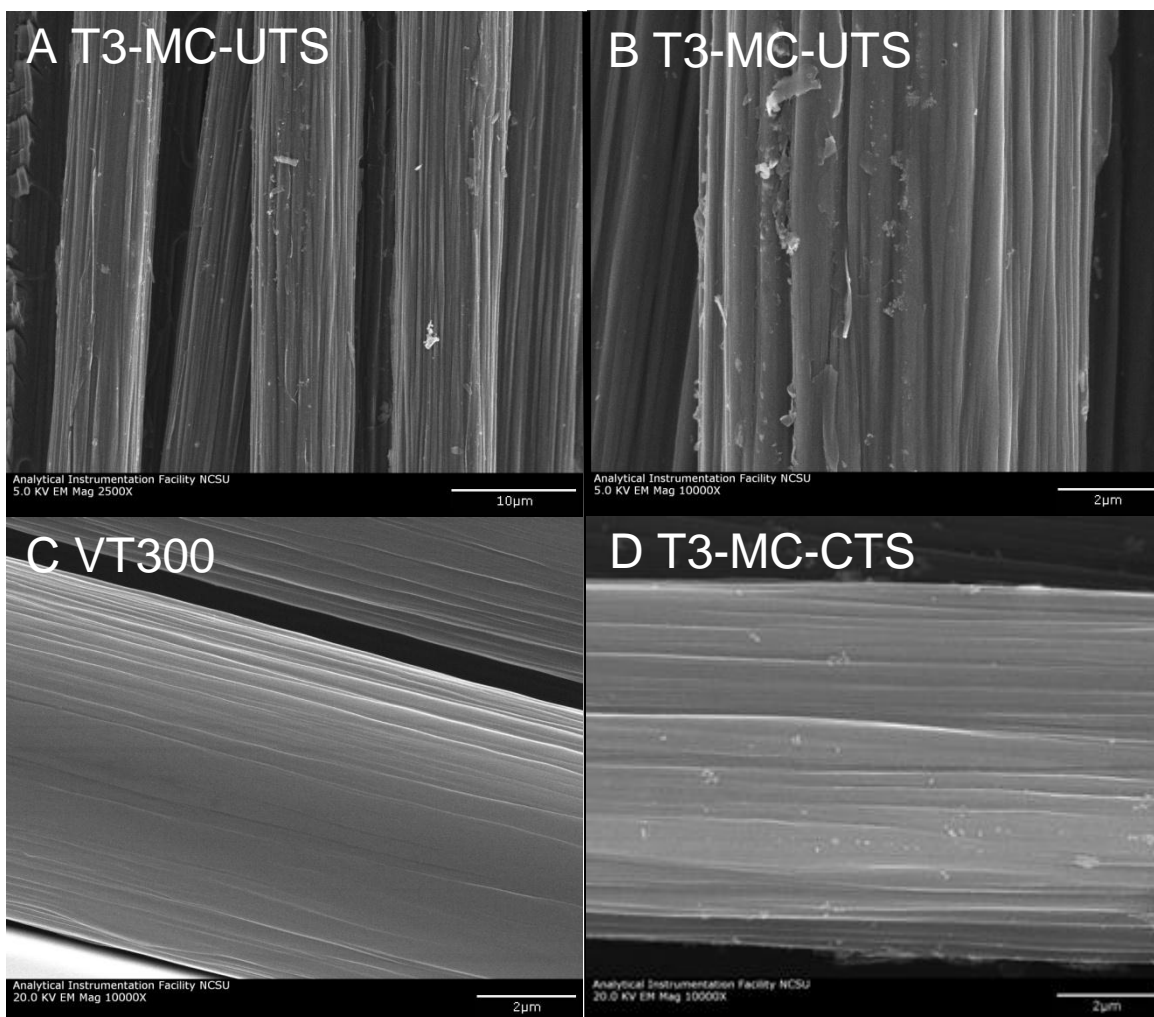
#### **3.4.2.D      *Cytec T300 Standard Modulus Fiber 6K Tow***

T300 fibers were recycled from two different material forms at two different times. Figure 3.6 shows SEM images of Virgin T300 and recycled T300 from uncured prepreg (VT300 and T3-MC-UTS respectively). The virgin sample, VT300 was obtained directly

from Cytec. T3-MC-UTS was sampled from a specific material batch at Boeing's Frederickson Washington Composites Manufacturing Center (CMC) with traceability to Cytec and subsequently recycled by pyrolysis in 2007. Figure 3.6a and Figure 3.6b show recycled T300 fiber at 5,000X and 10,000 x nominal magnification, respectively. These fibers were recycled in 2008 by pyrolysis from bulk uncured trim scrap material collected as part of a pilot study at the CMC.

The 2007 trial compares favorably to the virgin fiber image (Figure 6 d vs. c). The fiber surface crenulations appear slightly more pronounced for the recycled fiber however this may be due to variation. The 2008 trial (Figure 3.6 a and b) show significantly more drastic crenulations than the virgin fiber along with a large amount of flaky material on the surface of the fibers. Material sampled for the 2008 effort may have contained Toray T300 fiber vs. the virgin Cytec T300 fiber. This may explain in part or whole the morphology differences but at this time pyrolysis effects can not be ruled out. The flaking material on the surface of Figure 3.6a and Figure 3.6b may be residual resin char or partially disintegrated fiber material.



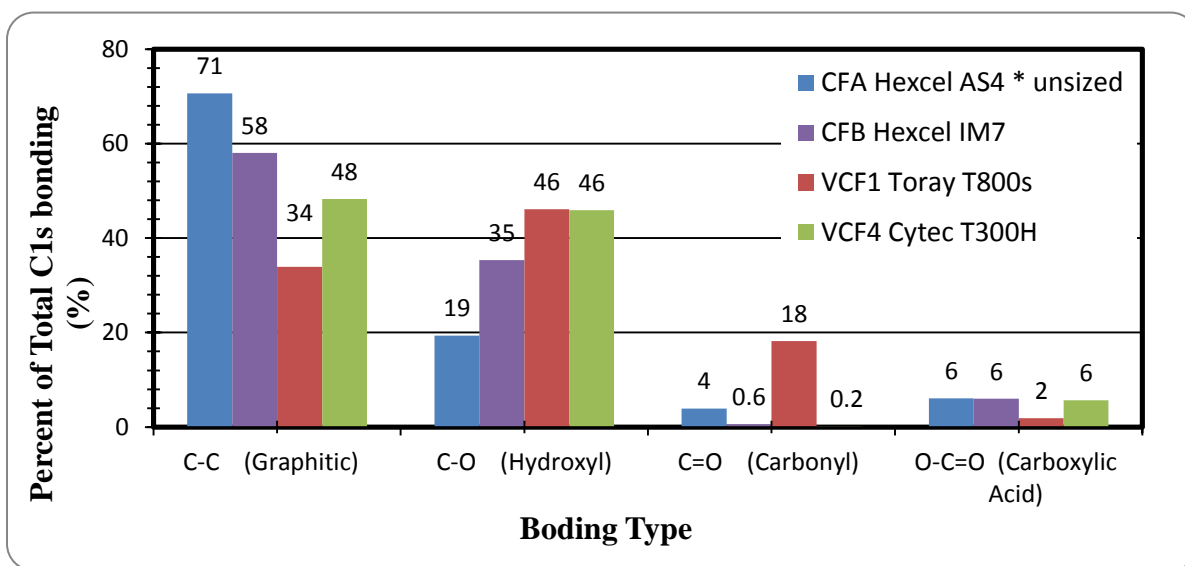


**Figure 3.6** Recycled and virgin T300 carbon fibers.

### 3.4.3 X-Ray Photoelectron Spectroscopy

To determine a reasonable baseline surface chemistry of virgin carbon fiber results from four fibers are shown in Figure 3.7. The Toray T800s and Cytec T300 fibers were obtained with a sizing on the surface which may explain then lower levels of observed graphitic bonding and elevated levels of carbon-oxygen bonding as detected by XPS.

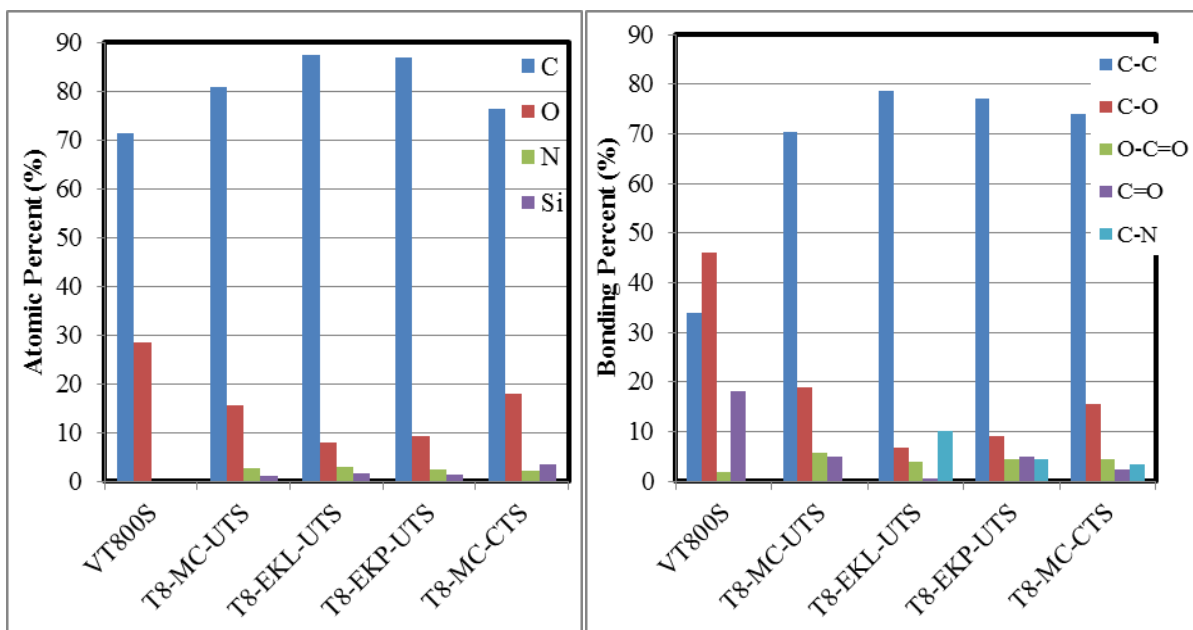
Unusually high oxygen to carbon atomic ratios were seen for the virgin T800s control fiber. This unexpected result can be attributed to a hydrocarbon size on the surface of the fiber.



**Figure 3.7 Comparison of bonding types on the surface of virgin fibers.**

Figure 3.8 summarizes the XPS atomic percent analysis for the T800s fibers studied and it is evident that in comparison to the control fibers, the recycled fibers have more carbon and less oxygen on the surface. Considering the control fiber is sized, it is difficult to tell what changes to the surface chemistry are made as a result of the recycling process. For a representative comparison data from the virgin unsized AS4 fiber can be used. Figure 3.8 also displays the results of XPS surveys collected from the carbon 1s binding peak. Carbon, oxygen, nitrogen, and silicon were found in the recycled fibers while only carbon and oxygen were seen in the control fiber. T8-EK(L)-CT and T8-EK(P)-CT look very similar to results from an unsized virgin carbon fiber. The fibers are primarily carbon (>80%) with a significant amount of oxygen. Carbon and oxygen are intrinsic to basic production of PAN precursor carbon fiber. The presence of silicon is harder to explain and may be introduced through use in composite structures and/or through the recycling process or by inadvertent contamination during handling.





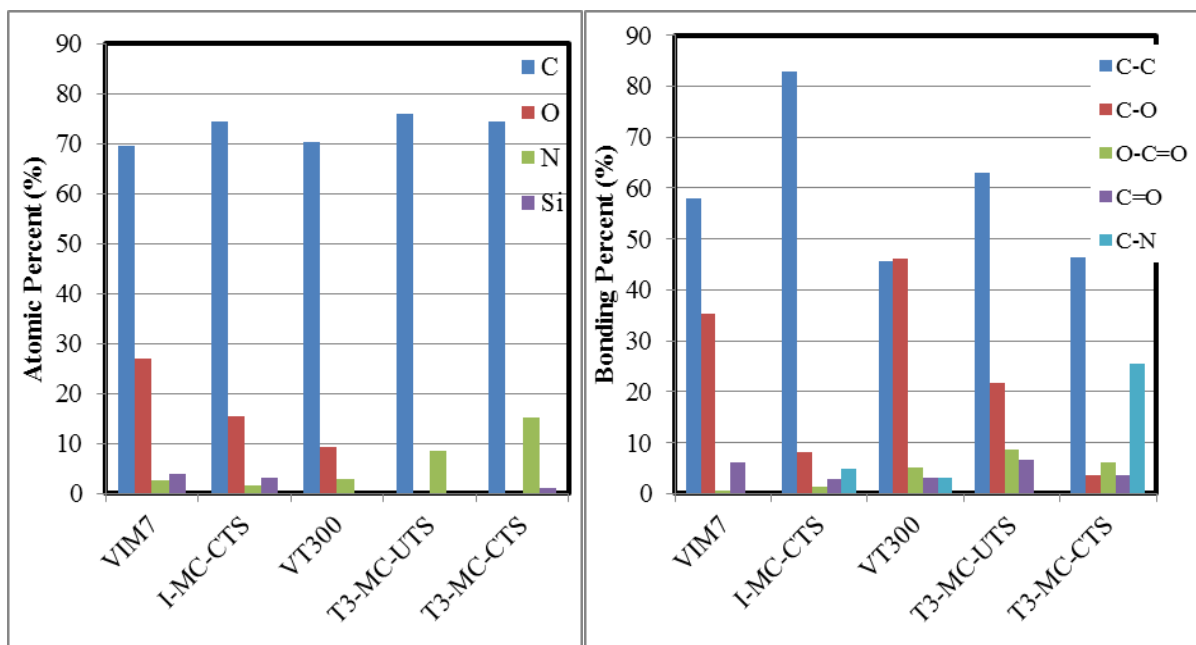
**Figure 3.8 Atomic percentages and bonding percentages for Toray T800s fibers.**

Since the virgin T800S fiber was sized the deconvolution of its carbon bonding was excluded from Figure 3.8. As expected, the recycled fibers have primarily graphitic bonding (C-C) with a fair amount of bonding involving oxygen containing functional groups. Figure 8 shows that T8-EK(L)-CT has about 10% of carbon-nitrogen bonding which is unusually high. Milled Carbon's T8-MC-CTS shows a considerable amount of hydroxyl (C-O) bonding which is consistent with the large amount of oxygen seen in the survey scan. Literature has shown large amounts of hydroxyl bonding can increase fiber to resin adhesion [70, 71] which is a topic to be discussed in conjunction with interfacial shear strength results presented in section 3.4.6.

Figure 3.9 shows the results of survey scans to detect atomic percentages on the surface of IM7 and T300 fibers. During NCSU's work in 2005, "VIM7" was provided as a virgin IM7 fiber and is shown in Figure 3.9 as the control sample for I-MC-CTS. I-MC-CTS, recycled from cured BMI composite in 2008, shows very similar surface chemistry to the IM7 control fiber. T3-MC-UTS is a Cytec T300 fiber recycled from uncured trim scrap and was studied by NCSU in 2007. T3-MC-CTS is a T300H fiber originating for either

Cytec or Toray and was recycled by Milled Carbon Ltd. on 1/8/2008 using the same process as was used for I-MC-CTS and T3-MC-UTS.

T3-MC-CTS and T3-MC-UTS have similar carbon contents, but T3-MC-UTS has a higher oxygen content while T3-MC-CTS has a higher nitrogen content. Both T3-MC-UTS and T3-MC-CTS had higher levels of nitrogen compared to the control fiber and a lower oxygen content than the control. These differences may be explained by the presence of sizing on virgin fiber, differences in recycling operations or differences in fiber manufacturer in the case of the T300 fiber. The XPS analysis of T8-MC-UTS and T3-MC-UTS did not include deconvoluting a C-N peak which is why no C-N bonding is reported in T3-MC-UTS even though significant levels of elemental nitrogen were seen.



**Figure 3.9 Atomic percent and chemical bonding percentages for IM7 & T300 virgin and recycled fibers.**

### 3.4.4 Single Filament Tensile Testing

#### 3.4.4.A Tensile Strength

Single filament tensile strength results for virgin and recycled T800s, T300 and AS4 fibers are shown in Figure 3.10 and Figure 3.11. Data labels showing percent strength retention for recycled fibers and showing actual values for virgin fibers. Lower values are expected from longer filament lengths as single filament strength is driven by flaw size and probability of occurrence. The fracture stresses for the virgin control fiber and T8-MC-UTS recycled fiber were linearly extrapolated and interpolated to gauge lengths of 6, 30, and 60mm from gauge lengths of 20, 50, and 100mm in order to attempt a comparison of test data from two different test sessions.

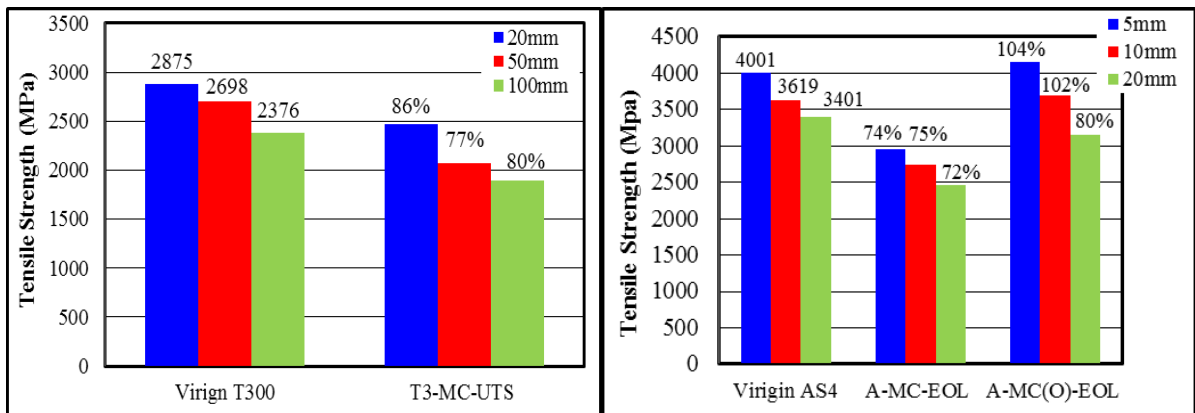
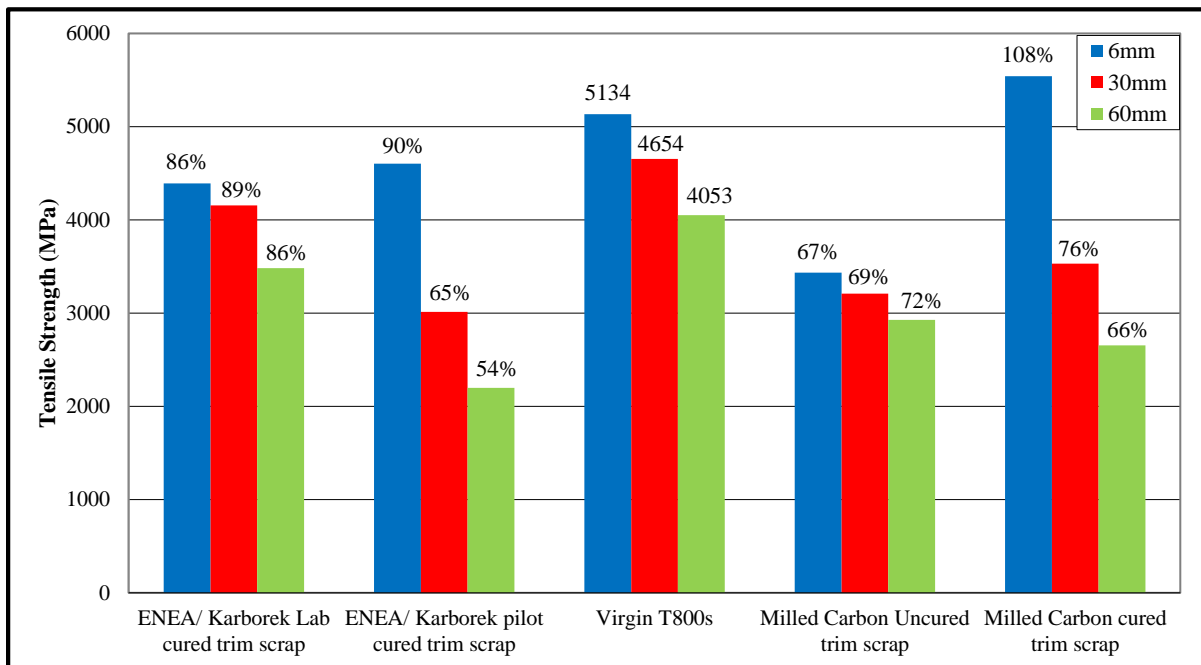


Figure 3.10 Tensile strength of virgin and recycled Cytec T300H and Hexcel AS4 fibers

Test results for the standard modulus fibers shown in Figure 3.10 exhibit good retention of strength especially for the A-MC-EOL-1 material. All standard modulus fibers shown were recycled by Milled Carbon Limited with A-MC-EOL-1 recycled after line condition optimization as compared to A-MC-EOL. T3-MC-UTS was recycled from uncured prepreg samples as compared to the A-MC-EOL and A-MC-EOL-1 samples which were recycled from end of life composites. The A-MC-EOL-1 fibers exhibit comparable

strength to virgin fiber at all gage lengths. T3-MC-UTS maintained about 20% or better of the strength of the virgin fiber samples at all lengths.

Test results for T800s intermediate modulus fibers show on average more reductions in strength as compared to the standard modulus fibers, more so at the longer gage lengths. This may be due to increased flaw sensitivity of the nominal 5 micron fibers. Also SEM micrographs shown previously do exhibit different degrees of fiber pitting as compared to virgin fiber which are most likely affecting filament strength. Note though that the lowest strength as measured at the 60 mm length for recycled IM fiber is comparable to virgin T300 50mm fiber strength as shown in Figure 3.10.



**Figure 3.11 Tensile strength of virgin and recycled Toray T800s carbon fibers.**

#### **3.4.4.B Tensile Modulus**

Figures 12 and 13 show modulus values calculated from data collected during single filament testing. One noticeable trend is the increase in modulus with increasing fiber length

for most samples. In all cases fiber modulus is reasonably close to the virgin fiber samples and vendor values.

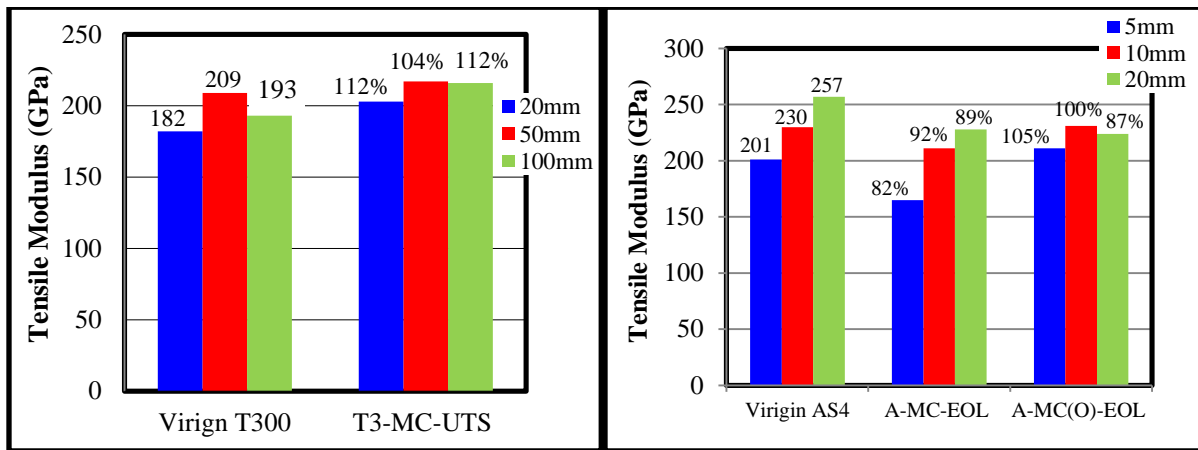


Figure 3.12 Elastic Modulus of T300 and AS4 fibers

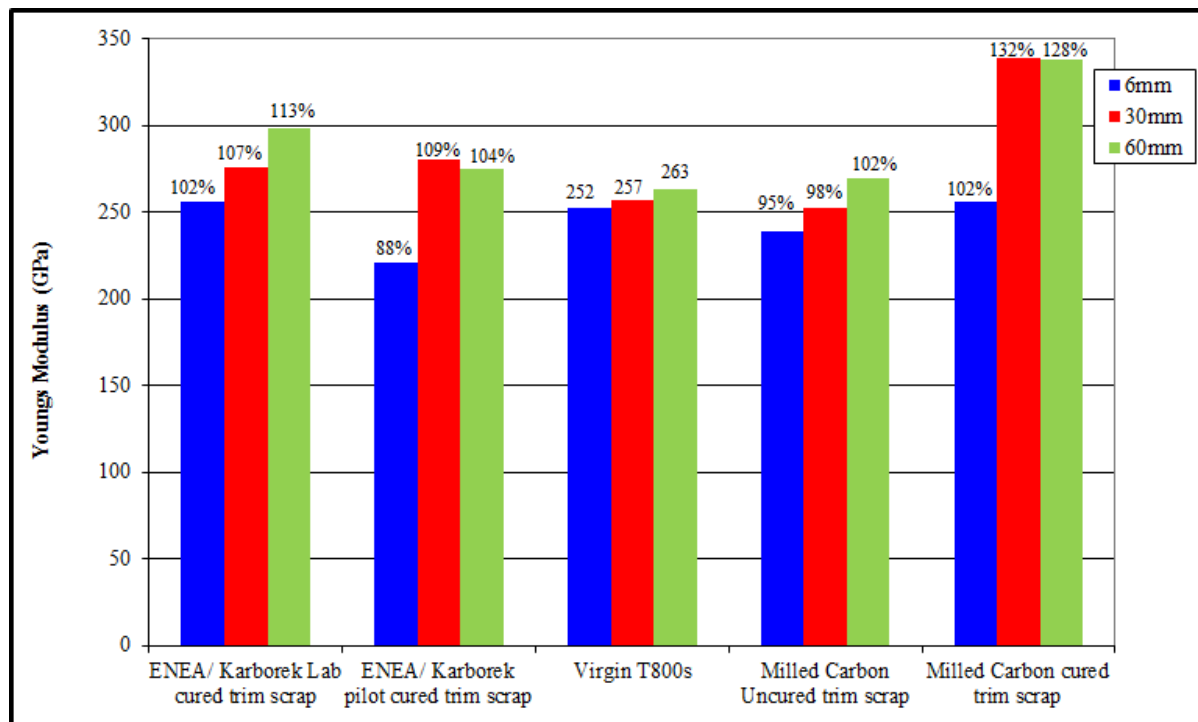


Figure 3.13 Tensile modulus of virgin and recycled Toray T800S fibers.

### 3.4.5 Single Fiber Composite Testing (SFC)

Figure 14 shows resin to fiber adhesion test results with Interfacial Shear Strength (IFSS) plotted vs. fiber type. Approximately 80-120 fragment lengths were generated and measured for each specimen over a 19 mm gauge length. The apparent interfacial shear stress of CF 4 was significantly less than the virgin fiber. After process optimization by Milled Carbon the IFSS of the recycled fiber (A-MC-EOL-1) was comparable to virgin fiber. T800s intermediate modulus fibers T8-EK(L)-CT, 6 & 7 show a considerable increase in IFSS while the standard modulus AS4 and T300 fibers show comparable or reduced performance. These improvements for the IM fibers may be due to increased surface roughness as observed in electron micrographs. The presence of debris, particulates and differing surface chemistries may also be playing a role in the observed differences in apparent interfacial shear strength.

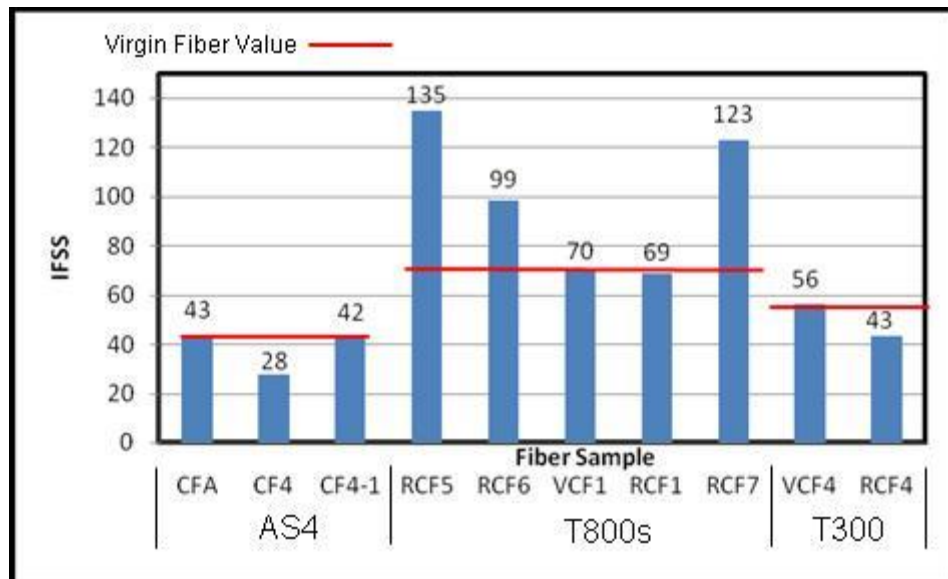


Figure 3.14 Summary of all IFSS testing grouped by fiber type.

### 3.5 Conclusions

IMST/NCSU evaluated eleven third party recycled carbon fibers provided by Boeing for their quality and appearance using scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), single filament tensile testing, and single fiber fragmentation interfacial shear strength measurements. Both standard modulus (SM) and intermediate modulus (IM) class fibers were recovered from a variety of resins and forms including cured and uncured materials. Virgin fibers were also included for comparison.

In general the recovered fibers compared favorably with the virgin fibers in appearance and performance. There were no statistically significant reductions in fiber diameter however averages were lower for IM fibers. For some of the SM fibers average diameters were larger for the recovered fiber compared to virgin indicating that these fibers may still have some resin char on the surface. Electron microscopy does show some residue on fiber surfaces but was not able to determine if this residue was resin char or decomposing fiber material. SEM images do show apparent fiber pitting and erosion to some extent for all the recovered IM fibers. In all cases various degrees of residue was seen in SEM images. Surface chemistry measurements by XPS indicated significant surface activity for resin interaction.

Comparison to virgin fiber was difficult in most cases due to the presence of epoxy based sizing agents. Also, for some fibers significant quantities of nitrogen were seen which could be coming from the pyrolysis process or residue from nitrogen containing amine components of the epoxy matrix resins.

The observed fiber surface morphologies may be affecting fiber strength and resin adhesion as indicated by tensile and fiber fragmentation tests respectively. Reductions in strength for SM fibers are less apparent than for IM fibers. For both SM and IM fibers modulus retention is excellent. Apparent interfacial adhesion strength for IM fibers was as good as or better compared to virgin fiber. Intermediate fiber surface morphologies observed may be providing more mechanical interlocking with the matrix resin. Conversely the residue seen on the surface of the SM fibers may be reducing adhesion. These test results are very promising as they show recycled fibers to retain most if not all the performance of virgin fibers. In the case of strength reduction for IM fibers their

performance is still comparable to or better than that of virgin SM fibers. As the large majority of structural carbon fiber in use today is standard modulus fiber the majority of the recycling process development work and optimization has most likely been based on this fiber class. Results here indicate significant fiber morphology changes for IM class fibers which may be affecting strength performance. Industry exploration and optimization of processes for recovering segregated, graded IM fiber feed forms is needed. With increasing use of IM fibers for applications such as the Boeing 787 and Airbus A350XWB clean, segregated IM factory excess feed forms will be available. Accompanying IM fiber optimized recycling processes will enable higher performance, higher value recycle.

The authors would like to thank Adherent Technologies, Milled Carbon Limited, and ENEA/Karborek for recycled carbon fiber samples for this study.



**4. A Comparison of Chemical, Morphological, and Mechanical Properties of Carbon Fibers Recovered From Commercial Recycling Facilities**

Joseph P. Heil, Davis R. Litzenberger, Jerome J. Cuomo

North Carolina State University

911 Partners Way

Raleigh, NC 27695-7907

*Manuscript to be submitted to the Journal of Advanced Materials*

## **4.1 Abstract**

Carbon fiber reinforced polymer composites (CFRPs) are highly desired materials exhibiting superior strength to weight properties. The main drawback to CFRPs is their high cost. The value of carbon fiber, along with the volume of manufacturing excess and end of life material, make recycling of carbon fiber an economically viable prospect in addition to an environmental responsibility. There has been a growing interest in using recycled fibers in non structural applications or applications where high thermal and electrical conductivity are desired. For the past four years North Carolina State University has evaluated recycled carbon fiber from lab scale and pilot plant operations from multiple companies such as Recycled Carbon Fiber, LTD and Adherent Technologies. Within the last year, commercial scale carbon fiber recycling operations have been started and the properties of carbon fiber reclaimed from these facilities were evaluated. The material reclaimed was from Boeing 787 production. Special attention was paid to recycled intermediate modulus (IM) fibers versus virgin standard modulus (SM) fibers, as previous work has shown better or comparable mechanical properties from recycled IM fibers compared to virgin SM. Similarly, X-Ray Photoelectron Spectroscopy (XPS) was used to assess changes in surface chemistry as a result of recycling, while Scanning Electron Microscopy (SEM) was used to review any physical damage or morphological changes. The fibers evaluated were recovered as part of a process baseline and oven location study; no process optimization was conducted prior to analysis of these fibers.

## **4.2 Introduction**

Carbon fiber recycling presents a cost recovery opportunity through recycling both manufacturing waste and end of life (EOL) aircraft. Carbon fiber composites enable lighter weight structures, reducing fuel burn per passenger mile. Additionally, carbon fiber components are less susceptible to corrosion and fatigue than aluminum, reducing maintenance costs, and enabling better cabin environmental conditions. The Boeing 787 Dreamliner, which took its first flight in 2009, consists of greater than 50% by weight carbon fiber reinforced epoxy composite. The Airbus A350 XWB, entering the detail design phase

and scheduled for 2013 delivery, also uses greater than 50% by weight carbon fiber reinforced epoxy. Between them, Boeing and Airbus have orders for over 1500 aircraft which will have wings, fuselage and empennage components made mostly of carbon fiber reinforced materials.

Boeing has been an industry leader in encouraging carbon fiber recycling through the development of the Aircraft Fleet Recycling Agency (AFRA), and funding recycled carbon fiber testing and analysis. AFRA's goal is the "sustainable management of end-of-life airframes and engines. AFRA collates, consolidates, promotes and publishes the collective experience of its members in its best management practice guides, which have significantly improved the management of end-of-life aircraft in terms of environmental and sustainable performance." Testing and analysis of recycled carbon fiber must be conducted to determine suitable applications, which include comparing recycled carbon fiber test results to virgin carbon fiber (VCF) control samples.

Recycled carbon fiber has a resell value based on its properties and potential applications. In previous years The Institute for Maintenance Science & Technology at North Carolina State University (IMST/NCSU) and Boeing have published test results on fiber from pilot scale recycling facilities operated by Adherent Technologies, Recycled Carbon Fibre Ltd. (Formerly Milled Carbon Ltd.), and ENEA/Karborek [30, 31, 35]. Future recycled carbon fiber analysis is related closely to demonstrating applications where recycled carbon fiber can be used. Recycled Carbon Fibre Ltd. mills woven material to be used as fillers, while unidirectional fabrics are cut to desired lengths [72]. Materials Innovation Technologies (eMIT) uses their recycling plant to provide fiber for their Three Dimensional Engineered Preform (3-DEP) process which can be used to make complex shapes. eMIT demonstrated that their process worked well for virgin chopped carbon fiber, and since recycled carbon fiber is already in chopped form and has about the same mechanical strength at short lengths, recycled carbon fiber provides a significant cost advantage without sacrificing performance [40, 73]. Injection molding would be an effective composite fabrication process for chopped recycled carbon fibers, but most recycling processes do not produce free flowing fibers that can be fed and metered into an extruder, making injection molding difficult. Table 4.1 lists both recycled and virgin fibers evaluated. RCF14, 15, and

16 were part of a process space location study recently completed where samples were run at different locations within the process. RCF17 through 19 are control samples respectively.

**Table 4.1 Overview of fibers evaluated**

<b>Fiber Code</b>	<b>Fiber Type</b>	<b>Source</b>	<b>Recycler</b>	<b>Year Tested</b>
V T300	T300	Cytec Virgin Fiber	N/A	2007
V T700G	T700G	Toray Virgin Fiber	N/A	2007
T3-MC-CTS	T300	Uncured Fabric	Milled Carbon	2008
T3-MIT-CTS	T300	Uncured Prepreg Fabric	eMIT	2009
T7-RCFL-UTS	T700G	Uncured Prepreg Fabric	Recycled Carbon Fibre	2009
RCF12	unidentifiable	Uncured Prepreg Fabric	Undisclosed	2009
RCF13	unidentifiable	Uncured Prepreg Fabric	Undisclosed	2009
V T800s	T800s	Toray Virgin Fiber	N/A	2007
T8-MC-UTS	T800s	Uncured Uni-Tape	Milled Carbon	2007
T8-MC-CTS	T800s	Cured Trim Uni-Tape	Milled Carbon	2008
RCF14	T800s	Uncured Prepreg Trim Scrap	Recycled Carbon Fibre	2009
RCF15	T800s	Uncured Prepreg Trim Scrap	Recycled Carbon Fibre	2009
RCF16	T800s	Uncured Prepreg Trim Scrap	Recycled Carbon Fibre	2009
VCF17	T800s	Extracted from T800s prepreg	N/A	2009
VCF18	T800s	Extracted from T800s prepreg	N/A	2009
VCF19	T800s	Extracted from T800s prepreg	N/A	2009

\* End of life F18 Stabilator

### 4.3 Experimental Procedure

IMST/NCSU's characterization procedure includes Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), single fiber tensile tests. Table 4.2 below shows the information gained from each test.

**Table 4.2 Summary of characterization techniques**

<b>Technique</b>	<b>Information Determined</b>
SEM Scanning Electron Microscopy	Fiber diameter, contamination Surface texture, defects
EDS Energy Dispersive Spectroscopy	Elemental composition of bulk
XPS X-Ray Photoelectron Spectroscopy	Atomic Percent, %'s of Carbon Bonding
Tensile Test	Fiber Tensile Properties, Weibull Shape & Scale Parameters

#### **4.3.1 Scanning Electron Microscopy (SEM)**

A Hitachi S-3200 variable pressure SEM was used to capture low magnification images from 500-5,000X for fibers studied in 2009. This particular microscope helped give an overall perspective of the fiber set. To gain a more detailed image of the fibers, a JEOL 6400F field emission SEM was used to obtain high magnification/resolution images. For RCFs 14-16, VCFs 17-19, VT800s, and VT300, the JEOL 6400F was used to take images at 500X-50,000X magnifications. RevolutionSEM by 4pi Analysis was used for data acquisition.

#### **4.3.2 Energy Dispersive Spectroscopy (EDS)**

An Oxford Isis EDS system was used in conjunction with the Hitachi S-3200 SEM. By bombarding the carbon fibers with an electron beam and collecting the x-rays, relative elemental presence was determined.

#### **4.3.3 X-ray Photoelectron Spectroscopy (XPS)**

A Riber XPS was used for VT800s and VT300 while a Kratos Analytical Axis Ultra XPS with a spot size of 300 $\mu$ m x 700 $\mu$ m was used for fibers studied in 2008 and 2009. Both instruments utilized Monochromated Al K- $\alpha$  radiation. Four specimens were analyzed for

each fiber sample. A complete scan was conducted on each carbon fiber sample, and the elemental peaks were identified along with their atomic percents.

#### **4.3.4 Single Fiber Tensile Testing**

Single fiber tensile testing from the VT300 fiber was done at the Cornell University Department of Fiber Science under the supervision of Dr. Anil Netravali. The fiber diameter was measured using an optical microscope and filar ocular lens. Tensile tests were performed on an Instron Universal tester (Model 5566). All tests were run at 0.4/minute strain rate. Fibers were tested at three different gauge lengths during each testing session. In 2009 single filament tensile testing was done according to JIS R 7601 using a constant rate of extension of 2.5mm/min on an Instron Universal Testing Machine Model 5544. Single filaments were mounted to cardstock with an opening cut out to set the gauge length at 6mm (0.25in) and 25mm (1.0 inches). Lines were printed on the cardstock to show the intended axis of testing and positions for clamping. A sufficient number of specimens were tested per fiber sample and gauge length so that outlier data points could be removed and at least 40 data points were left to contribute to the tensile property calculations. Tensile strength data was fit to a two parameter Weibull distribution to obtain the Weibull scale parameter (stress at which 63% of specimens failed) and the Weibull shape parameter (a measure of failure rate with increasing stress) [74].

### **4.4 Results & Discussion**

#### **4.4.1 Scanning Electron Microscopy - Fiber Diameter**

Images used for fiber diameter measurements were taken using a JEOL 6400F Field Emission SEM. These images were then processed using RevolutionSEM software. The photos were loaded using the software, and the “Measure” tool in Revolution was used to make diameter measurements which are listed in Table 4.3. VCF17, 18 and 19 were recovered using Soxhlet extraction from the same style of prepreg that RCFs 14-16 were recycled from. Obtaining control samples in this way enables testing of a control fiber without needing to trace the origin of scrap and obtain a material data sheet to identify the

correct fiber used in the composite. An increased fiber diameter with respect to a control fiber could indicate remaining resin on the carbon fiber whereas a decrease in fiber diameter could be evidence of oxidative damage to the fiber surface. Table 4.3 shows the average, standard deviation, and coefficient of variation for each fiber sample.

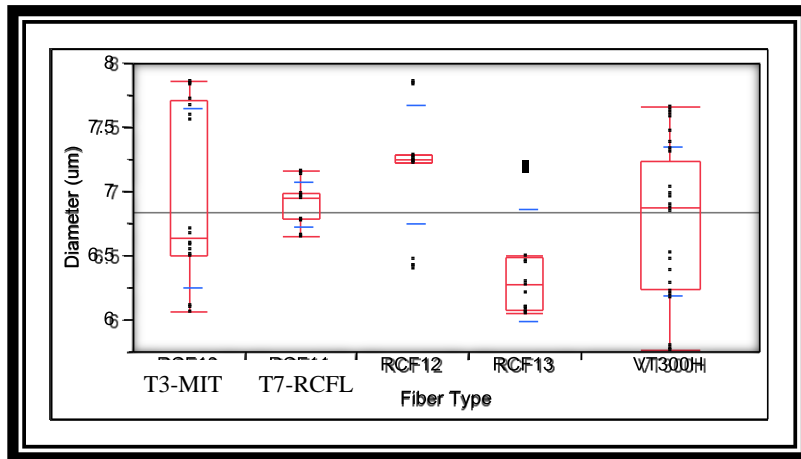
**Table 4.3 Fiber diameter measurements.**

Fiber Type		Fiber Code	Average ( $\mu\text{m}$ )	Stdev ( $\mu\text{m}$ )	CV (%)
<b>Intermediate Modulus</b>	Toray T800s	VT800s	5.37	0.313	5.8
	Toray T800s	VCF19	5.37	0.171	3.1
	Toray T800s	VCF18	5.50	0.184	3.4
	Toray T800s	VCF17	5.39	0.140	2.6
	Toray T800s	RCF16	5.49	0.248	5.2
	Toray T800s	RCF15	5.42	0.196	3.6
	Toray T800s	RCF14	5.43	0.227	4.2
<b>Standard Modulus</b>	Cytec T300	VT300	6.77	0.580	8.6
	Toray T700G*	VT700G	6.60	0.166	2.5
	unknown	RCF13	6.42	0.440	6.9
	unknown	RCF12	7.21	0.464	6.4
	Toray T700G	T7-MIT-UTS	6.91	0.175	2.5
	Toray or Cytec T300	T3-MIT-UTS	6.95	0.695	10.0

\*diameter measured using optical microscope

Figure 4.1 and Figure 4.2 show the output of a means comparison test from SAS JMP Statistical Discovery software that determines if differences in fiber diameter measurements from one sample to another are statistically different. A box plot display is overlaid over all the diameter measurement data points to show the sample mean (horizontal red bar in each box plot), standard deviation (narrow blue lines), and outliers (points outside the overlaid box plot). The ordered letter report in the table portion of Figure 4.1 indicates that only RCF13 is significantly different from the other SM recycled fibers. However, a large

number of outliers are seen in the box plot display indicating that more fiber diameter measurements should be made to ensure the best possible comparison. There is significant scatter in the data for the RCF samples shown in Figure 4.1.

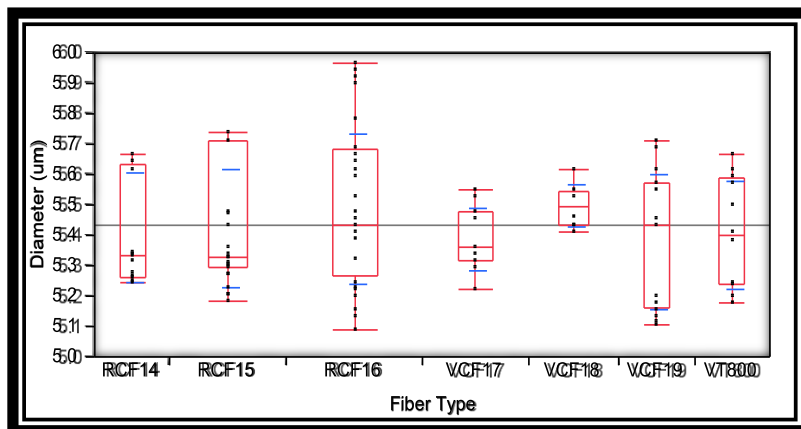


Comparisons for all pairs using  
Tukey-Kramer HSD

Fiber		Diameter ( $\mu\text{m}$ )
RCF12	A	7.21
T3-MIT-UTS	A B	6.95
T7-RCFL-UTS	A B	6.91
VT300	B C	6.77
RCF13	C	6.42

Levels not connected by same letter  
are significantly different.

**Figure 4.1 Means Comparison Test for Standard Modulus  
Fibers.**



Comparisons for all pairs using  
Tukey-Kramer HSD

Fiber		Diameter ( $\mu\text{m}$ )
VCF18	A	5.50
RCF16	A B	5.49
RCF14	A B	5.43
RCF15	A B	5.42
VT800	A B	5.40
VCF17	B	5.39
VCF19	B	5.38

Levels not connected by same letter  
are significantly different.

**Figure 4.2 Means Comparison Test for Intermediate Modulus  
Fibers.**

The measurements are bimodal which decreases standard deviation but increases the interquartile range of the measurements. The large range of diameters measured for VT300 makes it not significantly different from the other SM fiber samples except for RCF12. The

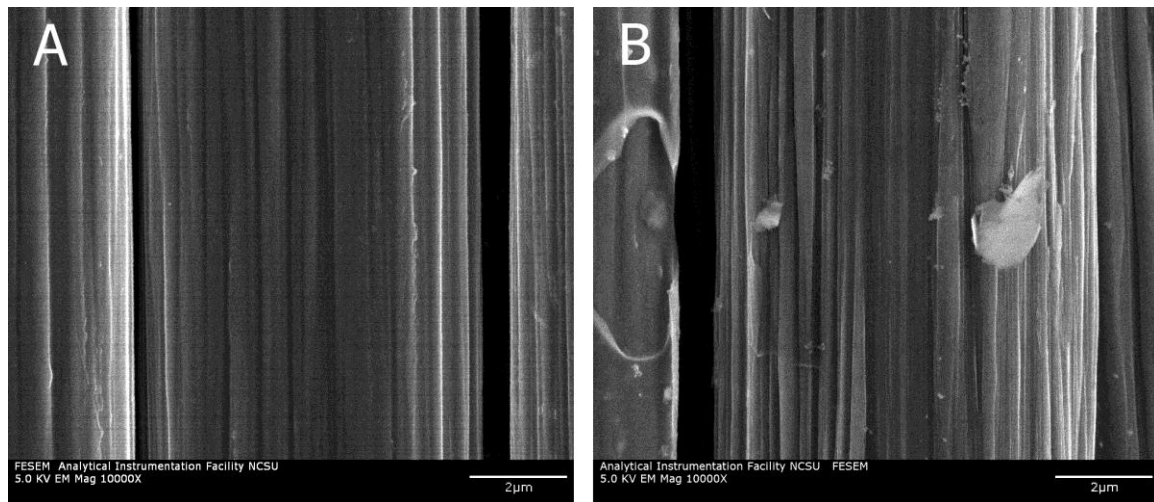


large range of diameter measurements on the VT300 fiber is in part due to its oval cross section. RCFs14-16 have standard deviations of around 0.2 $\mu$ m. As seen in Figure 4.2 there is no significant difference in fiber diameters between RCF14, RCF15, and RCF16.

#### 4.4.2 Scanning Electron Microscopy-Morphological Characterization

Fiber appearance before and after reclamation was evaluated using SEM with emphasis on changes in fiber surface morphology and residue or contamination. In previous work, differences in susceptibility to surface damage was noticed between recycled Standard Modulus (SM) class fibers (30-35 Msi) and Intermediate Modulus (IM) class fibers (40-44Msi) [35]. Similarly, the IM fibers in this study show pitting. While the SM fibers do not show evidence of pitting, the fibers have regions which have raised areas which may be incompletely pyrolyzed resin or have had the resin removed too aggressively leaving the fiber with a spongy appearance, with the exception of T7-RCFL-UTS. Incomplete pyrolysis of resin results in a carbon char which is difficult to chemically distinguish from the underlying carbon fiber.

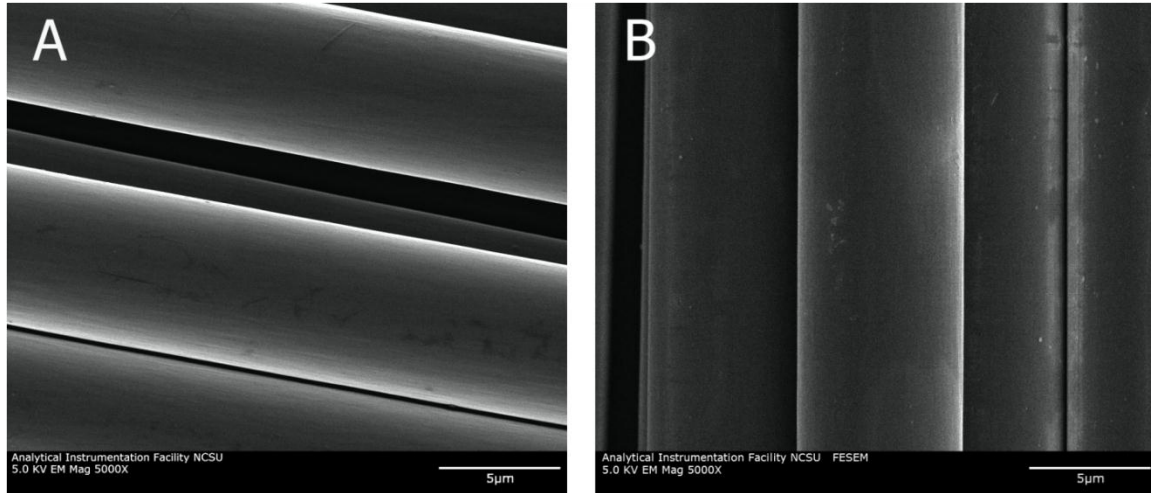
##### 4.4.2A Standard Modulus Fibers



**Figure 4.3** A) Virgin Cytec T-300 sample. Striations running the length of the fiber are clearly visible. B) T3-MIT-UTS-T300 fiber recovered from uncured prepreg.

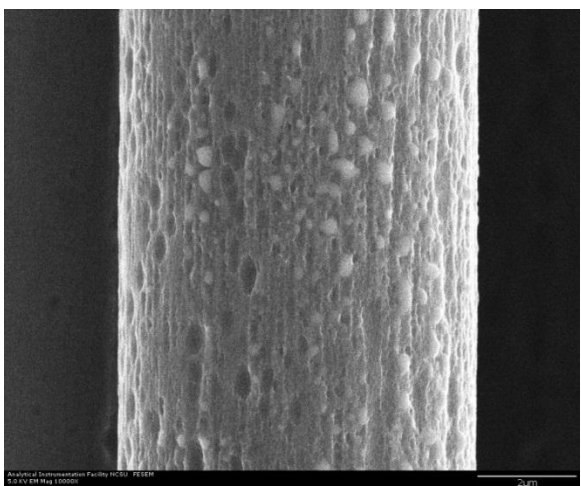
The T3-MIT-UTS fiber in Figure 4.3A appears as if there is a non-uniform coating on the surface of the fiber. T3-MIT-UTS has very noticeable ridge features running down the

length of the fiber as well as considerable debris on the fiber surface. This fiber sample appears very similar to the T300 cured trim scrap reclaimed by Milled Carbon, Ltd. in 2007.

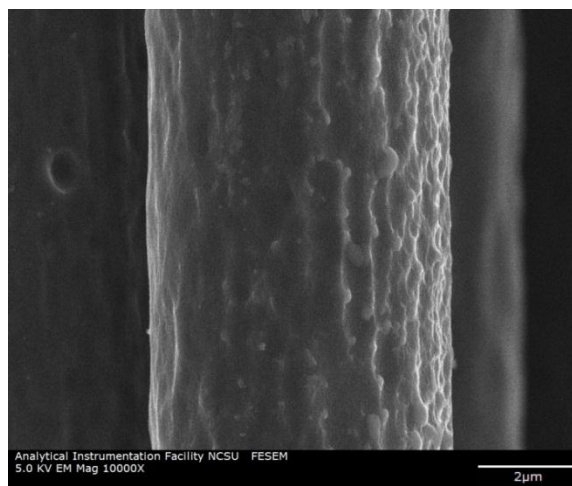


**Figure 4.4 A) Virgin T700G control sample.  
B) T7-RCFL-UTS fiber - recycled from T700G prepreg fabric.**

Figure 4.4B shows that T7-RCFL-UTS appears clean with minimal particulate matter adhered to the fiber much like the IM fibers studied in 2008. Figure 4.4A shows the control fiber for comparison. T7- RCFL -UTS still appears to be smooth like VT700G and the small amount particulate still adhered to the fiber becomes more noticeable when compared to the virgin fiber control in Figure 4.4A.



**Figure 4.5 RCF12- Mostly likely AS4 or T700G fiber but exact type could not be determined to degraded condition of fiber.**



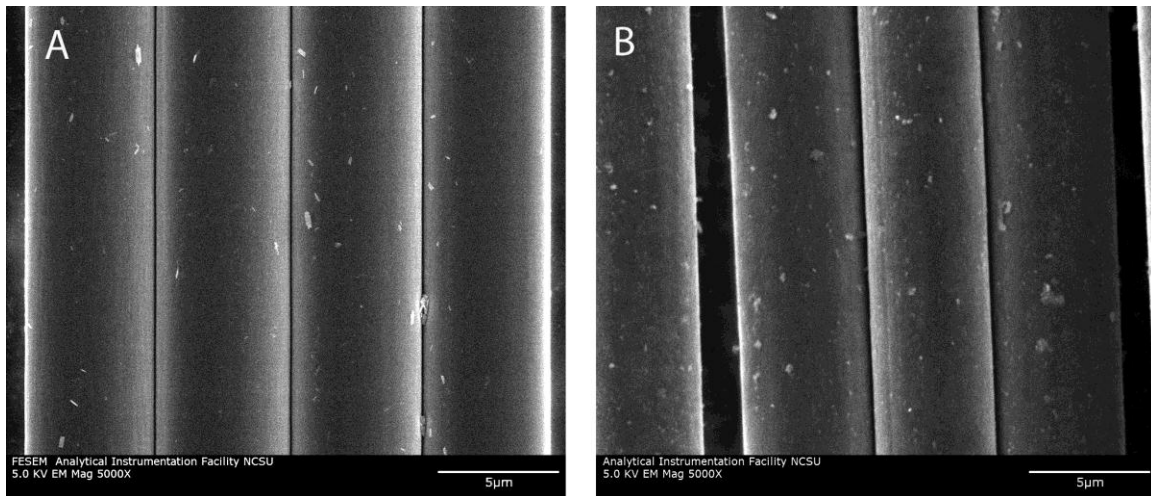
**Figure 4.6 RCF13 Mostly likely AS4 or T700G fiber but exact type could not be determined to degraded condition of fiber.**

Figure 4.5 shows more resin removal compared to RCF13, but large chunks of resin are clearly observed on the fiber surface. Additionally, the texture of the fiber appears grainy, which is evidence of defects caused by oxidation. Figure 4.6 shows resin that has not been completely removed from the surface of RCF13, leaving a spongy appearance. The spongy appearance likely comes as a result of the pyrolysis temperature during recycling becoming too high. A sudden rise in temperature causes the resin to flash burn instead of undergoing controlled thermal decomposition. This spike in temperature also makes the carbon fiber more susceptible to pitting by oxidation.

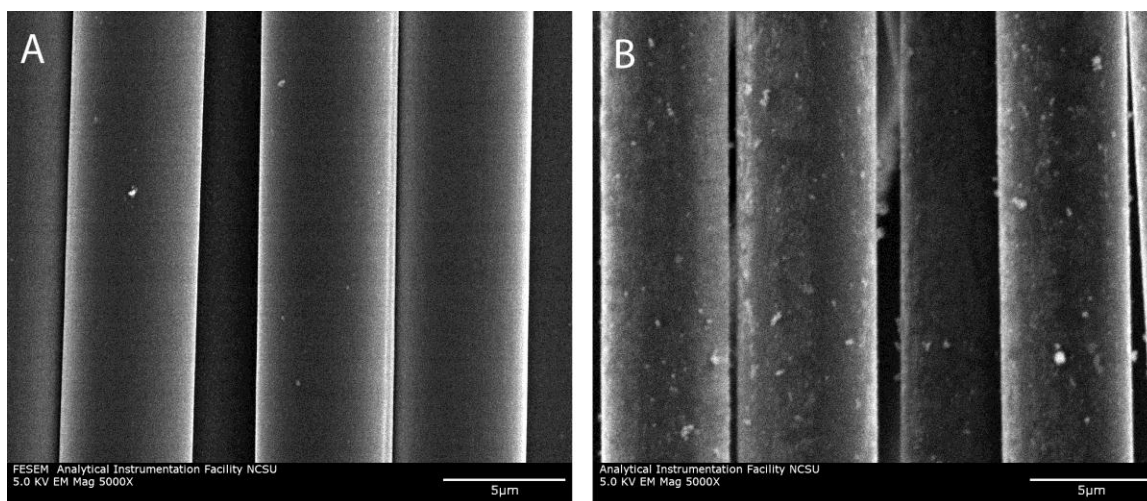
#### **4.4.2B Intermediate Modulus Fibers**

VCF17, VCF18, and VCF19 were supplied to NC State as prepreg samples to serve as control samples for RCF14, RCF15, and RCF16, respectively. Particulates or surface blemishes on VCF17, 18, or 19 are not representative of the fiber, but rather are artifacts from the soxhlet extraction procedure used by NC State to reclaim the fibers. Particulate matter on RCF14 is easily observed in Figure 4.7B. The amount of particulate matter is greater than that seen on T800s fiber recycled from cured trim scrap examined in 2008, but less than that seen on RCF15 and RCF16 in the 2009 series of fibers. Nearly all the particulates observed are less than 500nm in size. RCF14 fibers do not have any significant

morphology changes in comparison to control samples, although pitting is observed infrequently. In most cases RCF15 fibers seem to be forested with residual matrix material as seen Figure 4.8B. Energy Dispersive Spectroscopy shows trace concentrations of aluminum and silicon in the particulates. The fiber diameter was measured to be 5.32 $\mu$ m. The residual material on RCF15 is more in the form of a film or sporadic coating, not in the form of particles or chunks like in RCF14 and RCF16. Figure 4.8A shows VCF18: a fiber extracted from T800s prepreg for comparison. VCF18 has a smooth fiber surface as would be expected from an air gap spun fiber. No pitting or other evidence of oxidative damage was seen.



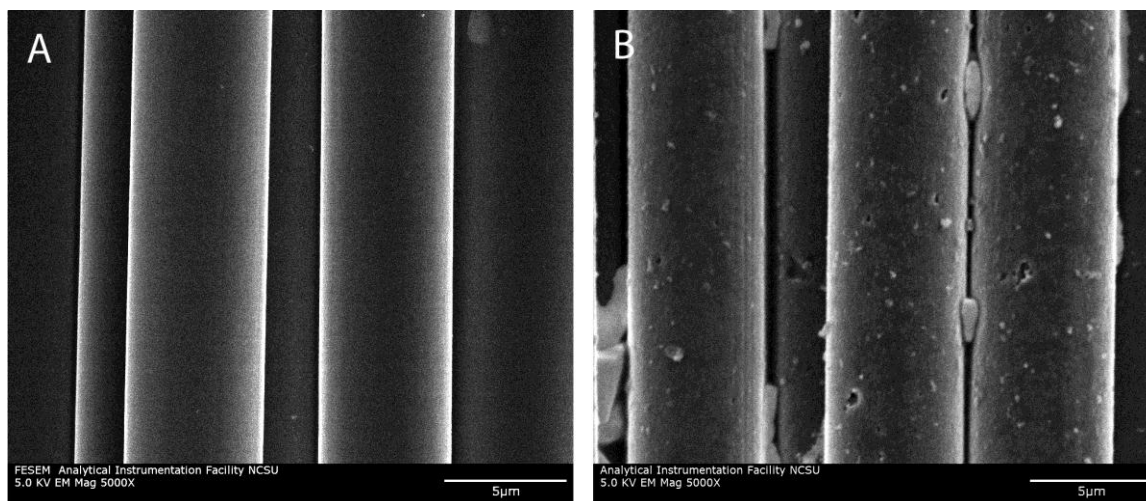
**Figure 4.7 A) VCF 17- obtained by soxhlet extraction. B) RCF 14-Particulates are clearly observable on fiber surface.**



**Figure 4.8 A) VCF 18- obtained from Soxhlet extraction. B) RCF 15 recovered from prepreg.**

In many instances RCF16 fibers (Figure 4.9B) have a hairy or fuzzy surface texture. This is best seen at 10,000x and higher magnifications since higher resolution is obtained using a Field Emission SEM. Figure 4.9A shows the VCF19 control fiber which has a smooth and clean surface. Minimal amounts of large (greater than 500nm) particulates were seen, although large accumulations of resin are seen in-between fibers (Figure 4.9B). Additionally, many RCF16 fibers are pitted with the overall frequency of pitting being greater for RCF16 than for RCF14 which would suggest the tensile strength of RCF16 to be less than that of RCF14.

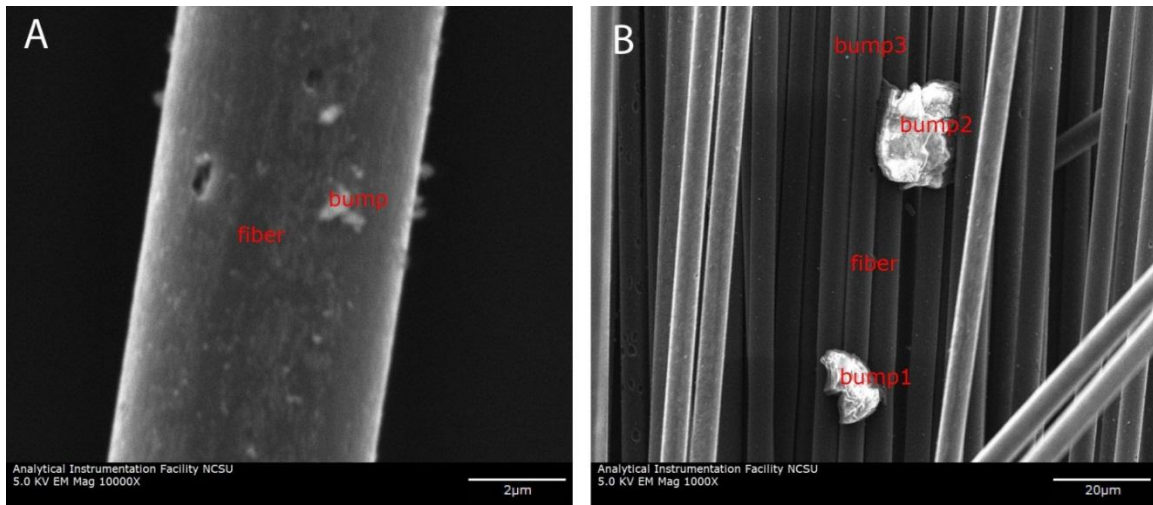




**Figure 4.9 A) VCF19-Recovered using soxhlet extraction. B) RCF16- Large chunks of resin remain in-between fibers.**

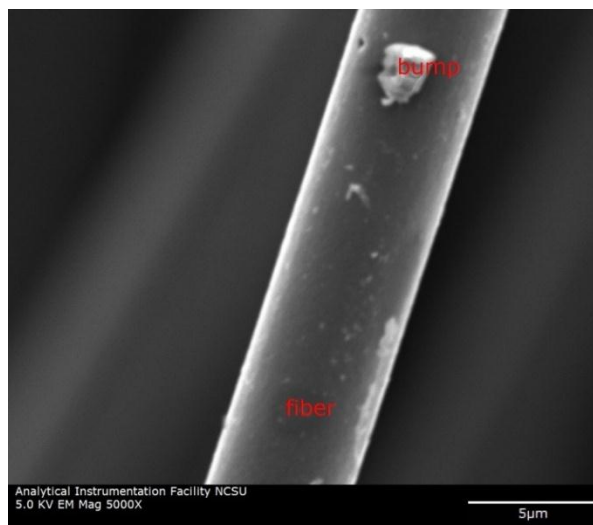
#### **4.4.3 Energy Dispersive Spectroscopy (EDS)**

EDS is used for a qualitative analysis of elements present in a material. The electron beam of the SEM is concentrated on an area within the sample which causes the sample to emit X-rays with a characteristic energy. The electron beam accelerating voltage was 5keV which allowed for a more localized analysis and minimizes the sampling depth of the electrons. An Oxford Isis EDS system was used in combination with the Hitachi S3200N SEM for this analysis.



**Figure 4.10 A) Reference image for EDS analysis of RCF14. B) Reference image for EDS analysis of RCF15**

EDS analysis of RCF14 shows only carbon and oxygen as part of the fiber. EDS analysis of the bump labeled in Figure 4.10A shows carbon, oxygen, and silicon. There is an increased amount of oxygen compared to the fiber itself, as well as the presence of silicon, both of which may indicate the presence of an epoxy matrix. Oxygen is found in the chemical structure of PAN even after it has been converted to carbon fiber. Silicon in the trace amounts seen could be from a filler material in the resin.



**Figure 4.11 Reference image for RCF16 EDS analysis**

Figure 4.10B shows several locations where EDS analysis was performed on RCF 15. The location labeled fiber showed only carbon and oxygen. The location labeled bump 3 has a silicon composition, while the location labeled “bump1” indicated the presence of sodium and chlorine. The EDS spectrum of the RCF16 fiber surface shows carbon and trace amounts of oxygen. The bump, as shown in Figure 4.11, shows carbon, large amounts of oxygen, and some calcium. Calcium may be a filler in the resin material or perhaps from a salt compound.

#### **4.4.4 X-Ray Photo Electron Spectroscopy**

Figures 4.12 and 4.13 summarize the XPS atomic percent analysis for both the SM and IM fibers using the VT300 as an SM control fiber. T3-MIT-UTS-RCF13 show slightly higher values of carbon and lower values of oxygen compared to the VT300 control. The VT300 fiber has an epoxy size on the surface which can increase the oxygen to carbon ratio compared to the bare surface. When comparing the recycled IM fibers to the virgin IM fibers, the relative amounts of carbon and oxygen detected is noticeably dependent on resin remaining on the surface. The Soxhlet extraction procedure used to recover VCFs17-19 uses hot sulfuric acid which could easily oxidize the carbon fiber surface, giving an increased O/C ratio such as shown in Figure 4.12 for VCF17.



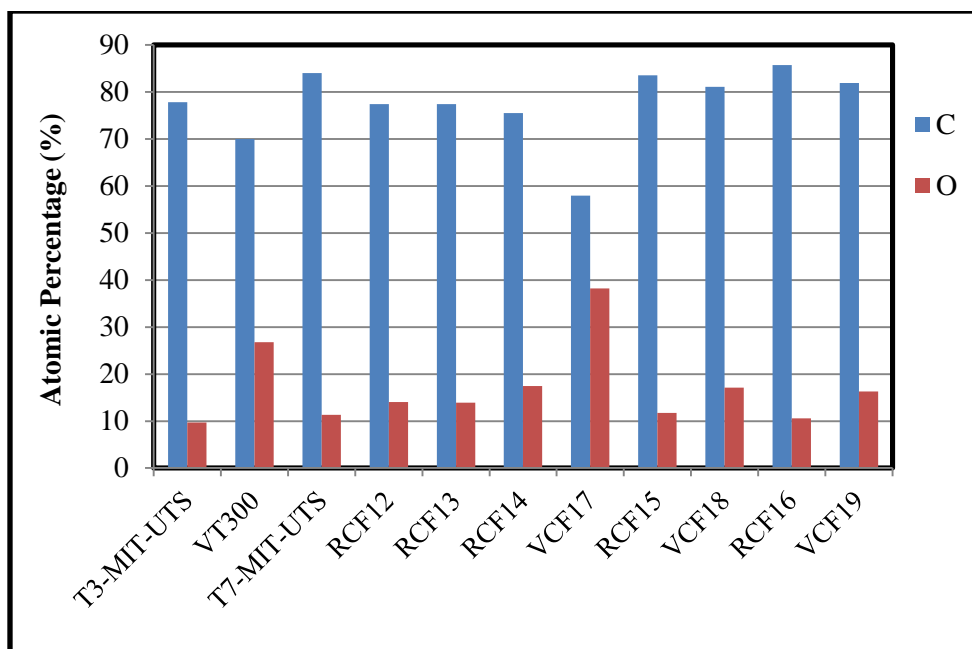


Figure 4.12 Atomic concentration of carbon and oxygen as measured by XPS.

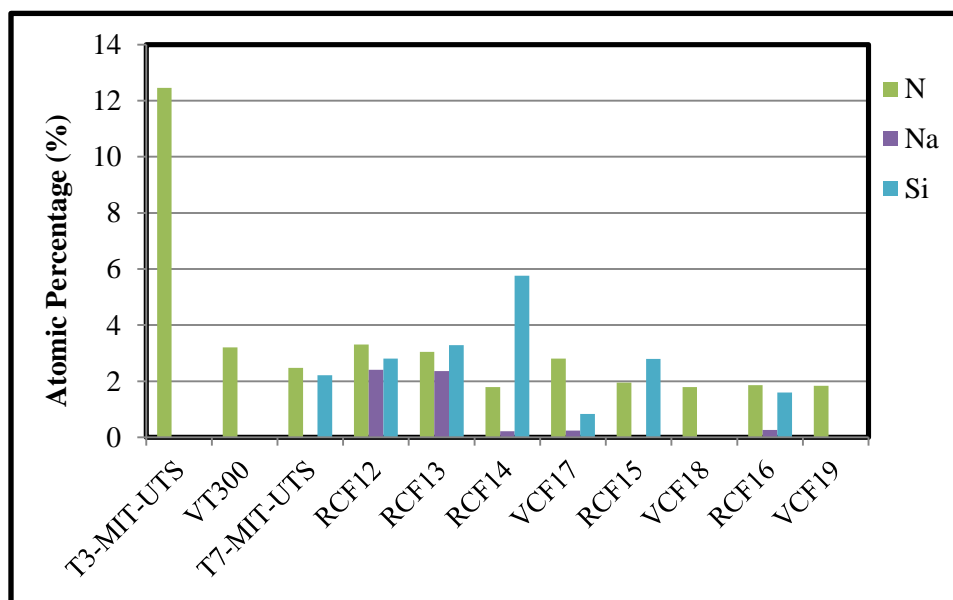


Figure 4.13 Atomic concentration of nitrogen, sodium, and silicon as measured by XPS

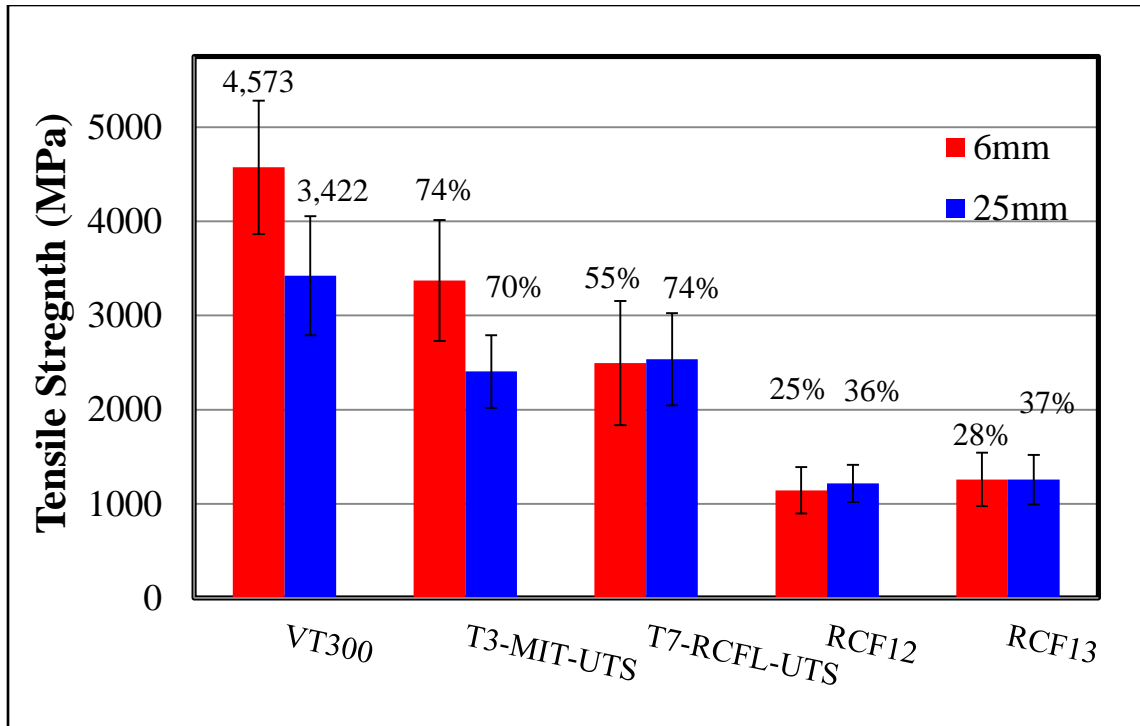
Figure 4.13 is a comparison of nitrogen and other elements that are probably contamination in the sense that they are not native to a carbon fiber surface. As expected, the

VCFs have little to no contamination in the form of silicon or sodium. Tin and copper were also observed in about half of the survey scans conducted, but the amounts were less than 0.5% and are excluded from the analysis shown in Figure 4.13. T3-MIT-UTS shows around 12% nitrogen on the surface, which is the largest amount of nitrogen seen by NC State on recycled carbon fibers. Nitrogen can come from a variety of sources, the most probable being as a result of a deliberate surface treatment and by an activated surface absorbing nitrogen from the atmosphere. Oxidizing carbon fibers creates active sites which will absorb gas species from the environment when high temperature pyrolysis is carried out in an inert atmosphere such as nitrogen. Silicon was seen on all recycled carbon fibers, except T3-MIT-UTS, and was also seen on VCF17, indicating silicon is incorporated into the resin. Sodium is not supposed to be seen on a clean carbon fiber surface, and its presence in both recycled and virgin carbon fibers suggests it came from the resin, as opposed to refractory materials such as furnace linings or contamination from handling. Silicon and sodium were seen in EDS analysis when a particulate was sampled but not when the clean portion of the fiber was sampled.

#### **4.4.5 Single Filament Tensile Test**

##### ***4.4.5A Tensile Strength***

Single filament tensile strength results for SM fibers are shown in Figure 4.14, while IM fiber results are shown in Figure 4.15. T3-MIT-UTS shows 70% strength retention at the 25mm gauge length with respect to VT300, which is poor with respect to results seen from pilot scale recycling facilities. At a 25mm gauge length T7-MIT-UTS has a slightly higher tensile strength, 2,503MPa, than T3-MIT-UTS. RCF12 and RCF13 have severely reduced tensile strengths at both 6mm and 25mm gauge lengths; which is consistent with SEM observations.



**Figure 4.14 Tensile Strength of Standard Modulus Fibers.**

Figure 4.15 shows strength retention at the 25mm gauge length for the recycled IM fibers is around 55% which is less than the tensile data on T800s fiber recycled in 2008. VCF17 and VCF18 have similar tensile strength to the VT800s fiber studies in 2008 which has a tensile strength of around 5100MPa at 6mm gauge length and 4600MPa at 30mm gauge length. RCF16 showed the greatest degree of pitting based on SEM imaging and is the weakest fiber at 6mm gauge length, as expected, but not at 25mm gauge length. RCF15 and RCF16 show increasing strength with increasing gauge length which is highly unusual for synthetic fibers. Figure 4.16 shows the results of a Means Comparison test using SAS JMP Statistical Discovery Software. A Means Comparison test performs multisample t-tests to determine which sample means are different from each other and also reports the value of each sample's mean (in the case the fiber's tensile strength). The Tukey-Kramer HSD (Honestly Significant Difference) method is used to determine which samples are similar and

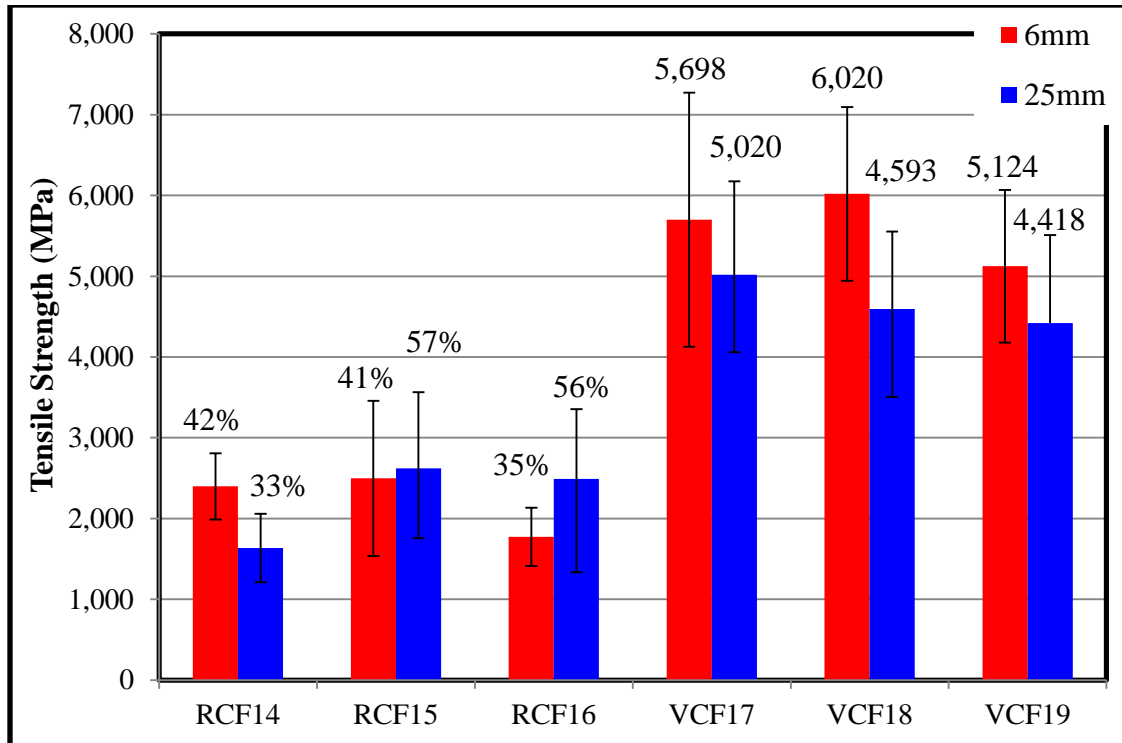


Figure 4.15 Tensile Strength of Intermediate Modulus Fibers.

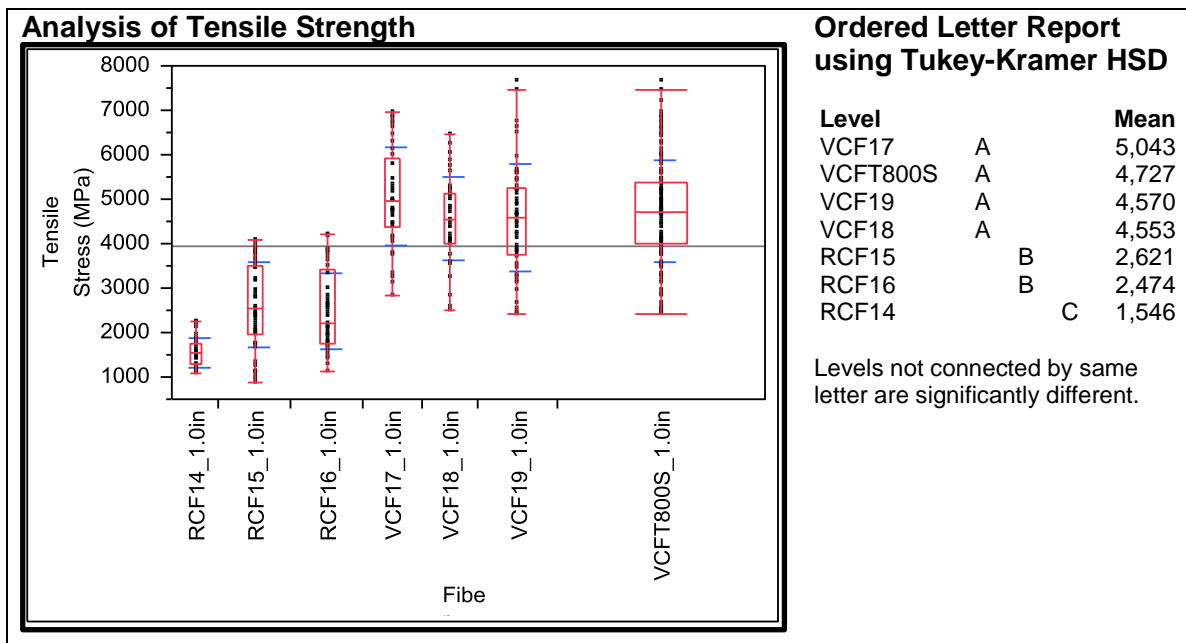
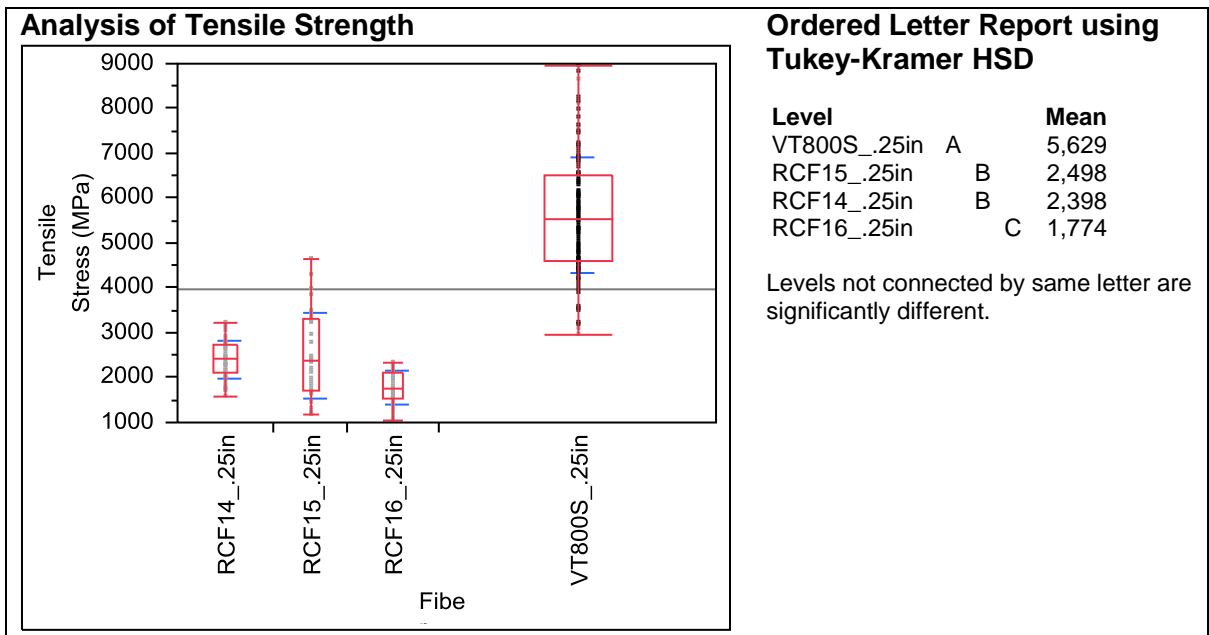


Figure 4.16 Means Comparison and Ordered Letter for Tensile Strength of IM fibers tested at the one inch gauge length. VCFT800S is the combined data of VCFs 17-19.

or significantly different. As shown in the order letter report each sample is assigned one or multiple letters. Samples that share a letter (s) are not significantly different. In Figure 4.16 all the recycled carbon fibers are significantly different from each and every virgin carbon fiber. RCF 14 is significantly weaker than RCF 15 and RCF 16. All four virgin fiber samples have a similar strength. JMP was used to remove outlier data points from the means comparison analysis which accounts for the differences is average tensile strength reported in Figure 4.15 and Figure 4.16.

The differences in tensile strength between RCFs 14,15, and 16 at the one-quarter inch gauge length as shown in Figure 4.17 are more consistent with expectations based on SEM observations where RCF 16 was heavily damaged by pitting. Obvious fiber morphology differences exist between RCF 14 and RCF 15 but at the quarter inch gauge length, unlike at the one in gauge length, these differences do not correspond to a difference in tensile strength.



**Figure 4.17 Means Comparison and Ordered Letter for Tensile Strength of IM fibers tested at the one quarter inch gauge length. VT800S is the combined data of VCFs 17-19.**

#### ***4.4.5B Tensile Modulus***

Figure 4.18 shows the elastic moduli of SM fibers while Figure 4.19 shows elastic moduli for IM fibers. At 6mm gauge length the T3-MIT-UTS is measured to be stiffer than the VT300 control, but the standard deviations are 18GPa for the VT300 fiber and 24GPa for T3-MIT-UTS which makes the difference in modulus less dramatic and not significantly different. Taking standard deviations into account the difference in modulus between the VT300 fiber sample and the T7-RCFL-UTS fiber sample is not significant. At 25mm gauge length the standard deviations of the elastic modulus are smaller and the difference in average elastic modulus between the VT300 fiber sample and the T3-MIT-UTS and T7-RCFL-UTS fiber samples is more pronounced. In prior work, the elastic modulus of a recycled fiber has been shown to be higher at the expense of reduced tensile strength [35]. The elastic modulus for all three recycled fiber is 80-90% that of the control fibers, except for RCF15 at the 6mm gauge length. For reference, the sized virgin T800s fiber sample has an elastic modulus around 255GPa which is much closer to the values calculated for RCFs 14-16. Overall the elastic modulus tests results indicate these fibers will perform nearly as well as virgin carbon fibers in high stiffness applications. Based on unusual trends in elastic modulus and tensile strength, it is clear that a further investigation into failure modes would be valuable.

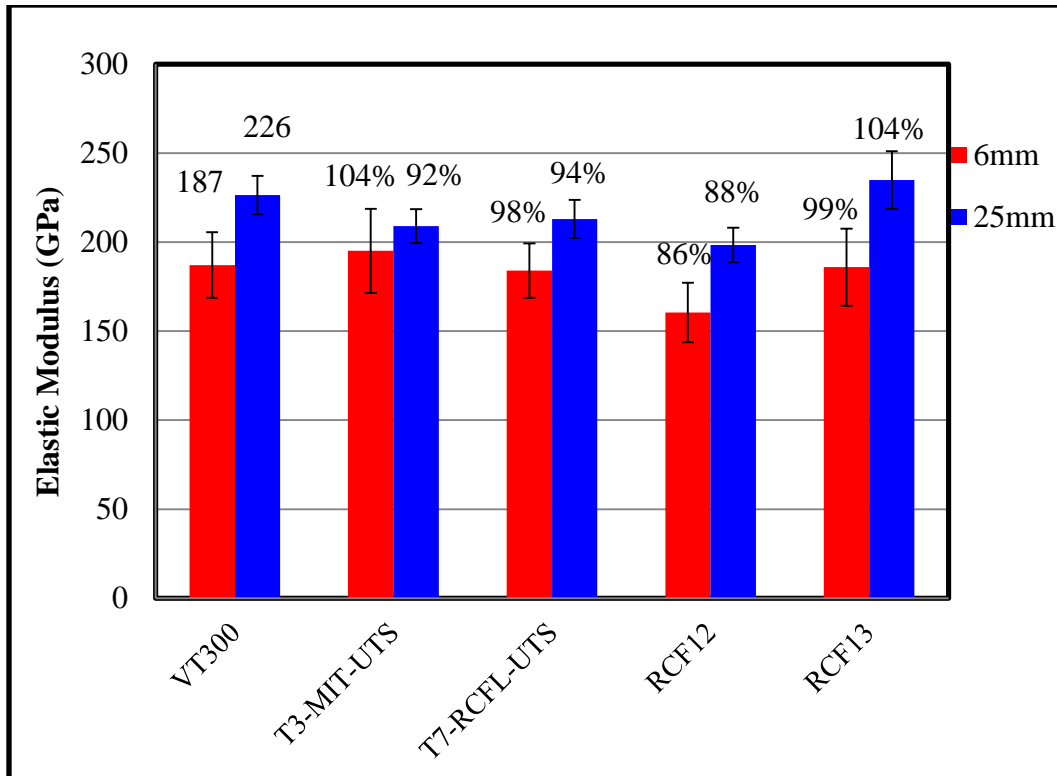


Figure 4.18 Elastic Modulus for Standard Modulus Fibers

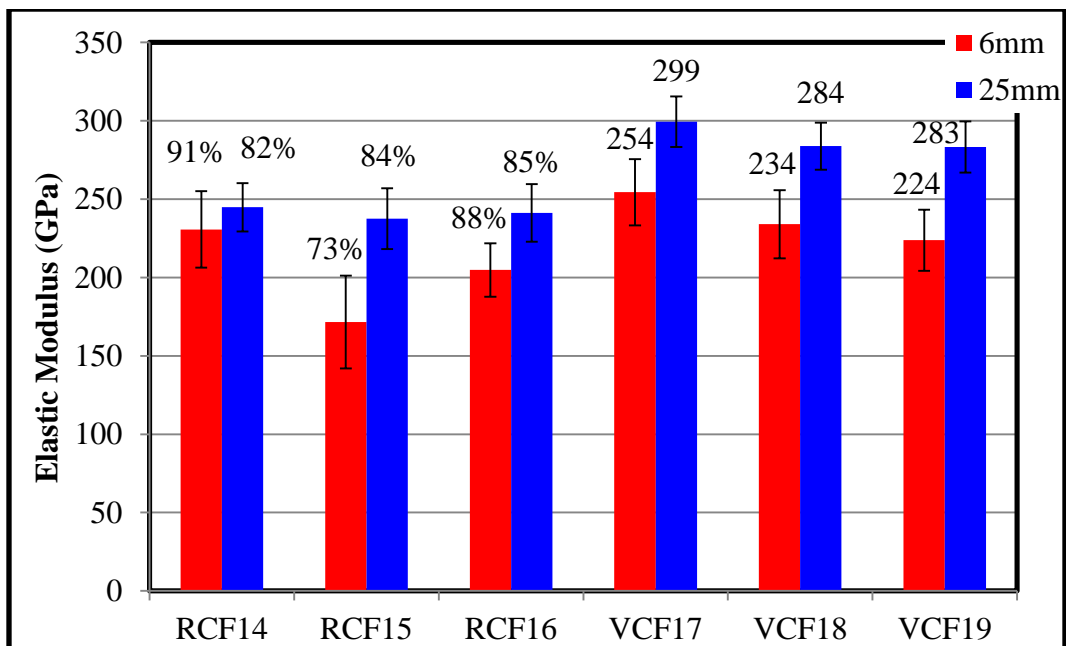
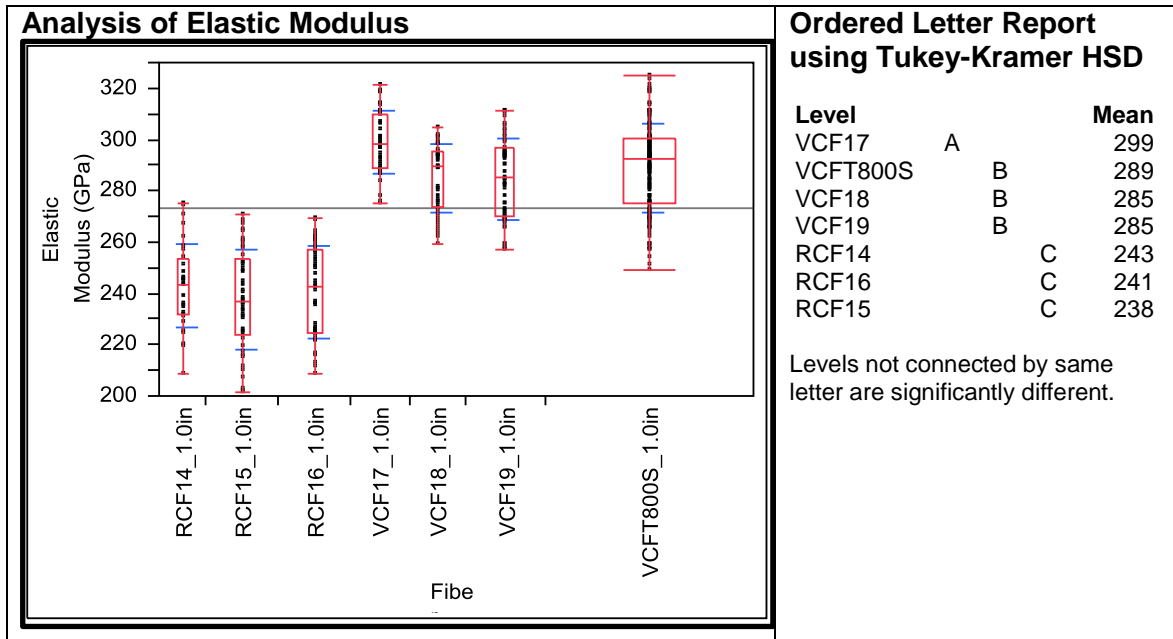


Figure 4.19 Elastic Modulus for Intermediate Modulus Fibers

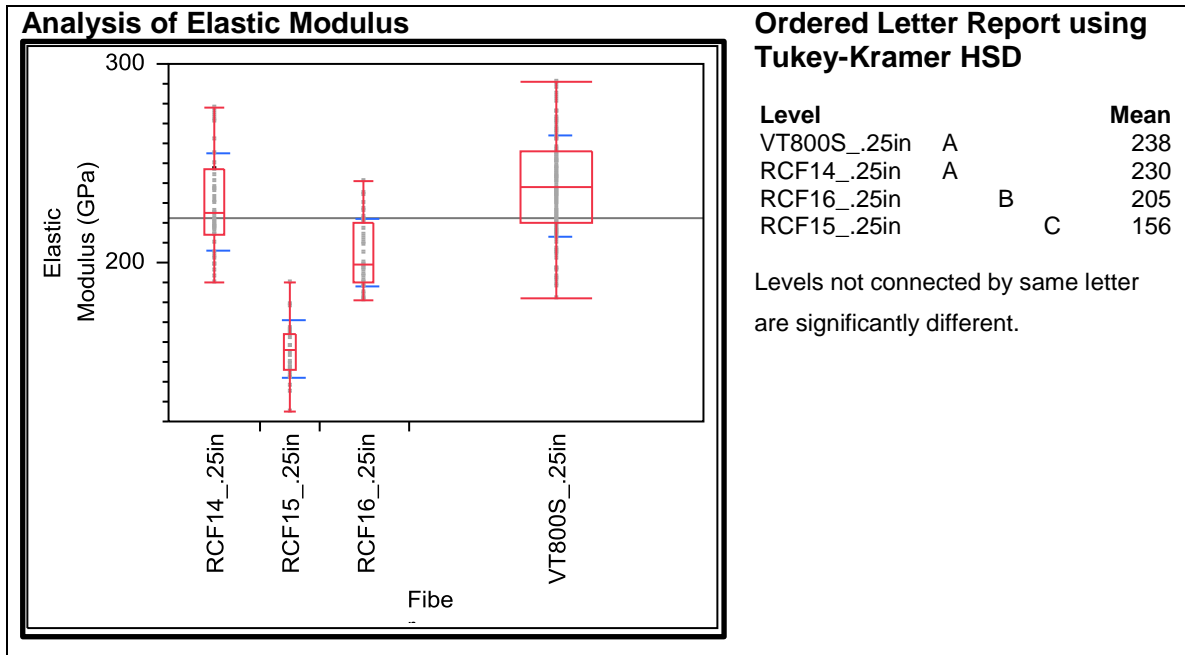


**Figure 4.20 Means Comparison and Ordered Letter for Elastic Modulus of IM fibers tested at the one inch gauge length. VCFT800S is the combined data of VCFs 17-19.**

Figure 4.20 shows a histogram comparison plot for the elastic modulus of IM fibers tested at the one inch gauge length and is accompanied by an ordered letter report showing which fibers are significantly different from each other. All the recycled fibers are shown to have a similar stiffness which is less than each and every virgin carbon fiber sample. VCF17 is reported to have a slightly higher elastic modulus than the other three virgin fiber samples.

Figure 4.21 is the same as Figure 4.20, but shows fibers tested at the 6mm/ one quarter inch gauge length. At the 6mm gauge length differences in the elastic modulus between fibers is more pronounced with RCF 14 being stiffer than RCF 16 which is stiffer than RCF 15. RCF 14 is similar in stiffness to the virgin fiber data,





**Figure 4.21 Means Comparison and Ordered Letter for Elastic Modulus of IM fibers tested at the one-quarter inch gauge length. VT800S is the combined data of VCFs 17-19.**

## 4.5 Conclusions

IMST/NCSU evaluated seven third party recycled carbon fibers and three virgin carbon fibers provided by Boeing for their quality and appearance using scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and single filament tensile testing. Both standard modulus (SM) and intermediate modulus (IM) class fibers were tested. Fiber cleanliness and integrity are significantly less in comparison to recycled fiber tested from various facilities in 2007 & 2008. Most standard modulus and intermediate modulus fibers have residual matrix material as evident from SEM and XPS. Recycled fibers were evaluated with high end structural applications in mind. Fiber diameter measurements did not show significant differences compared to virgin carbon fibers. Substantial amounts of oxygen and nitrogen was found on the surface of recycled carbon fibers which suggests the opportunity for a high degree of resin to fiber adhesion. Sodium and silicon were also commonly seen as contaminants in the XPS analysis. Intermediate modulus fibers showed only 55% strength retention at 25mm gauge length single filament testing, however the

elastic modulus is comparable to virgin fiber. The frequency and severity of pitting revealed through electron imaging may be a cause for the observed reductions in tensile strength during single filament testing. Standard modulus fibers showed around 70% strength retention which is palatable, but less than that previously observed. Recycled carbon fibers are comparably stiff to their virgin fiber counterparts, which presents a cost savings opportunity over using virgin carbon fiber. Intermediate modulus fibers may fundamentally pose greater challenge for retention of strength during pyrolysis processing as compared to standard modulus fibers. Future work will include verification of these results and possibly process space exploration for optimization. Improvements in process parameter selection relative to fiber type as the recycling industry matures will hopefully result in higher IM fiber strength retention. This may open additional market opportunities where premiums are placed on fiber strength and stiffness.

The authors would like to thank the Boeing Company for their continued funding in support of recycled carbon fiber testing and analysis.

## **5. Composite Panels Made from the Wetlay Process Using Recycled Carbon Fiber**

Joseph P. Heil<sup>1</sup>, Jeffrey B. Gavin<sup>2</sup>, Pete E. George<sup>2</sup>, Jerome J. Cuomo<sup>1</sup>

<sup>1</sup>North Carolina State University Department of Materials Science & Engineering  
911 Partners Way  
Raleigh, NC 27695

<sup>2</sup>The Boeing Company  
9725 East Marginal Way  
Seattle, Wa 98108

*Manuscript to be submitted to the Journal of Advanced Materials*

## 5.1 Abstract

Carbon fiber reinforced polymer composites are highly desired, high value materials exhibiting superior strength to weight properties. The value of carbon fiber, along with the volume of manufacturing excess and end of life material, make recycling of carbon fiber both economically viable and environmentally responsible. One challenge in carbon fiber recycling is the identification of carbon fiber types. Factory scrap and end of life materials most often arrive at recyclers with no documentation differentiating standard modulus vs. intermediate modulus fibers. As a result these fibers may be blended downstream as a discontinuous reinforcement phase for composites with unknown effects on mechanical performance. A study where recycled carbon fibers are blended with virgin carbon fibers is needed to characterize the effects of recycled carbon fiber on mechanical properties, and to clear the way for recycled fiber to supplement virgin fiber offering cost savings with an understood trade off in performance.

In this effort, recycled carbon fibers were utilized in a wetlay process to make light weight randomly oriented fiber mats preforms. Fiber preforms were made by blending standard modulus and intermediate modulus carbon fibers of virgin and recycled quality. Our previous analysis [35] of recycled carbon fiber showed 80-90% strength retention at the 13mm gauge length compared to virgin carbon fiber. Composite panels molded from recycled carbon fiber offer a cost competitive alternative to sheet molding compounds (SMCs) made with glass fiber while maintaining comparable mechanical properties.

## 5.2 Introduction

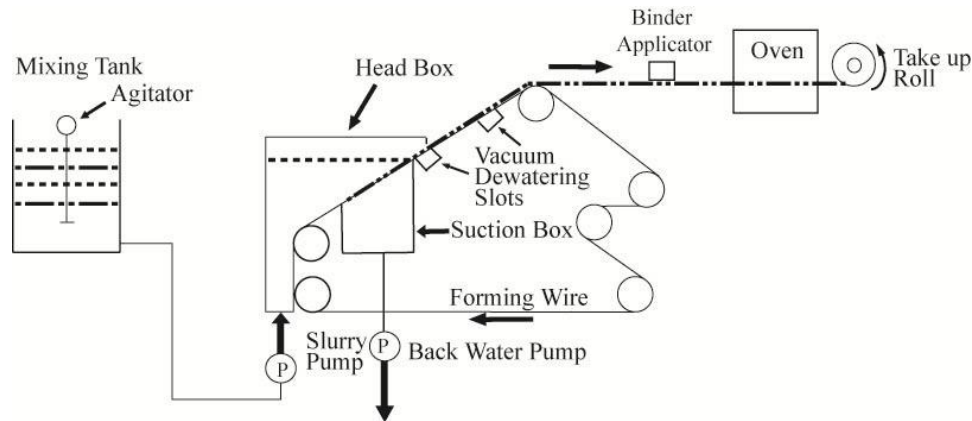
Bulk molding compounds (BMCs) and sheet molding compounds (SMCs) are prime products to replicate using recycled carbon fiber. Both BMCs and SMCs use short chopped fiber, have low to moderate fiber loading (25-50wt% for automotive BMCs and 50+ wt% for aerospace SMCs) are used in secondary structures, and are easy to manufacture. Most SMCs used in the automotive industry use glass fiber since carbon fiber is too expensive; however carbon fiber SMCs offer a 60% weight reduction compared to steel [23]. Instead of chopping continuous fiber and letting it fall onto a thin film of resin as in traditional SMC production,

resin transfer molding (RTM) was selected to make a recycled carbon fiber reinforced plastic (rCFRP) panel. Fiber mats were made using the wetlay process and then stacked to achieve an areal density of  $1500\text{g/m}^2$  to create a fiber preform that was placed in a closed mold connected to a resin transfer molding (RTM) machine. RTM is a process that injects resin into a closed mold containing the fiber reinforcement of a composite. The dimensions of the mold specify the dimensions of the composite panel. An injection system for RTM mixes resin and hardener (for 2 part systems) or mixes resin and catalyst (for a 1 part system) at a desired temperature to lower the resin viscosity. Vacuum is pulled on the exit outlet of the mold while resin is allowed to flow through and out of the mold removing any contaminants caught in the preform. The exit outlet is then closed and the RTM system pushes resin into the mold at a certain feed rate until a specified level of pressure is built up. As resin fills the mold cavity, it pushes back on the injection system creating the pressure that the injector feels. Once the desired pressure level is reached the injection system will administer more resin as needed to maintain constant pressure. As the resin cures it densifies, relieving pressure.

#### **5.1.1 The Wetlay Process**

The fiber preforms used as the reinforcement phase of the resin transfer molded panels were prepared using the wetlay process. The wetlay process is commonly used for making paper and non-woven mats from non-pulped fibers. Equipment similar to that used for paper making is well suited for making low areal weight fiber mats. As depicted in Figure 1, essential components of the equipment for forming carbon fiber mats are: mixing tank(s), a head box, inclined screen (forming wire), vacuum ports to suck out excess water from the mat, a pumping system, a binder applicator, and an oven to dry the mat. Forming of the mat is accomplished when fiber pumped into the headbox drifts onto the inclined screen. Generally the fiber lays onto the screen in a randomized fashion, however modifications to the equipment and process are possible to preferentially orient the fibers in the machine direction (direction of travel of the belt) [65, 68, 75]. Increasing belt speed will help increase orientation, but the flow rate would need to be adjusted to maintain the same areal weight. One limit to how heavy a mat can be made is the rate at which water can be drained from the

mat. Heavier mats hold more water and must be drained quickly and uniformly to maintain mat quality. Considering a randomly oriented carbon fiber mat made using an inclined wire machine, the maximum weight that can be realistically achieved is 40-60g/m<sup>2</sup>; by orienting the fiber, higher basis weights are achieved [65, 68, 75]. Also, machines that form the mat through a centripetal motion seem to be capable of higher basis weights without sacrificing quality [65, 68, 75].



**Figure 5.1 Wetlay Process for making fiber mats. Based on US Patent 5,409,573[76]**

Basis weights of 100g/m<sup>2</sup> in a single layer could be stacked to provide a preform with a similar bulk density as sheet molding compounds made from chopped virgin fiber. As areal weight increases, defects such as thick and thin spots as well as clumps and divots are more likely to be incorporated into the mat. Having thick and thin spots is not as much a concern as the clumps and divots when using this material in composites. Thick and thin spots tend to get evened out when multiple layers are stacked together. However, clumps and divots when stacked, form empty space or act as stress concentrators which lowers mechanical properties.

Through interactions with several companies specializing in the wetlay process (The Nonwovens Institute, Raleigh, NC; South East Nonwovens Inc, Clover SC; and Technical Fibre Products Ltd., Kendal, Cumbria UK) a more detailed understanding of the factors involved in the wetlay process has been learned. Obtaining a high degree of fiber dispersion is the most critical factor leading to high quality fiber mats. Fewer clumps in the final mat

and constant thickness/ areal weight across the entire mat are best obtained by maximizing dispersion in the mixing tank.

Agitation, white water chemistry, fiber surface chemistry, fiber length, and coatings on the fiber are all factors that must be optimized to achieve high degrees of dispersion without sacrificing processing time or fiber quality. Different propeller designs and speeds provide various levels of agitation; greater agitation often increases dispersion, but also reduces fiber length. Fiber length directly controls the maximum achievable strength and stiffness of composites with longer fibers making stronger & stiffer composites. Composites with fiber lengths in excess of 2.54cm (1in) can be simplistically viewed as having continuous fiber reinforcement. Longer fibers are more likely to get entangled with fibers of shorter lengths and clump up when being laid on to the screen. Many pumping systems have a maximum allowable fiber length of 2.54cm (1in) to prevent fibers from stopping up the pump. Not only is having fibers that are too long decrease uniformity, but having a wide fiber length distribution also increases the tendency of fibers to tangle and clump. Viscosity modifiers and surfactants are two types of chemicals often added to the water to make up the “white water chemistry”. Each company has a different recipe and even then additional amounts of chemicals are added to the water until the slurry looks right. Viscosity modifiers are used to homogenize the flow of the slurry, while surfactants change the surface energy of the water to better match the fiber surface chemistry, in effect dissolving the fibers. Without excellent fiber dispersion needed to achieve a very high degree of uniformity in the fiber preform, the molded composite will contain defects that compromise its strength.

## **5.2 Experimental**

The purpose of this study was to investigate mechanical properties of composites made with a blend of recycled carbon fiber (RCF) and virgin carbon fiber (VCF). SMCs are a potential product where a VCF/RCF blend can be utilized commercially. Since SMC production is expensive to do on a lab scale, RTM was selected as the composites molding process. Recycled T800S (R-T800S), intermediate modulus fibers, obtained from Recycled Carbon Fiber Ltd. (West Midlands, UK) were used as the recycled fiber material in this

blending trial. Initially aerospace grade AS4 standard modulus (SM) and IM7 intermediate modulus (IM) carbon fibers from Hexcel Corporation were selected as two types of virgin fiber to be used in the blending trial. The binder applied to these fibers by Hexcel was not water soluble or easily removed using chemical or thermal treatments, making dispersion of these fibers extremely difficult. A standard modulus VCF commonly used in the wetlay process, Sigrafil C30 (SGL), was selected to be blended with the recycled T800S fiber. Southeast Nonwovens also had a difficult time dispersing the R-T800S fibers and used a heat treatment in an attempt to remove residual matrix or char on the fibers. The heat treatment was conducted in a kiln used to heat air to 620°C and then held at temperature for 1 hour. Samples of the fiber after one heat treatment cycle and after two heat treatment cycles were saved for further analysis. R-T800S fibers used in the wetlay process underwent two heat treatment cycles. Table 5.1 gives an overview of important properties of fibers considered for use in the wetlay process. Tensile properties of the recycled T800S fibers used were not measured, so virgin T800S and a previous characterization of recycled T800S fibers from Recycled Carbon Fiber, Ltd. is presented in Table 1.

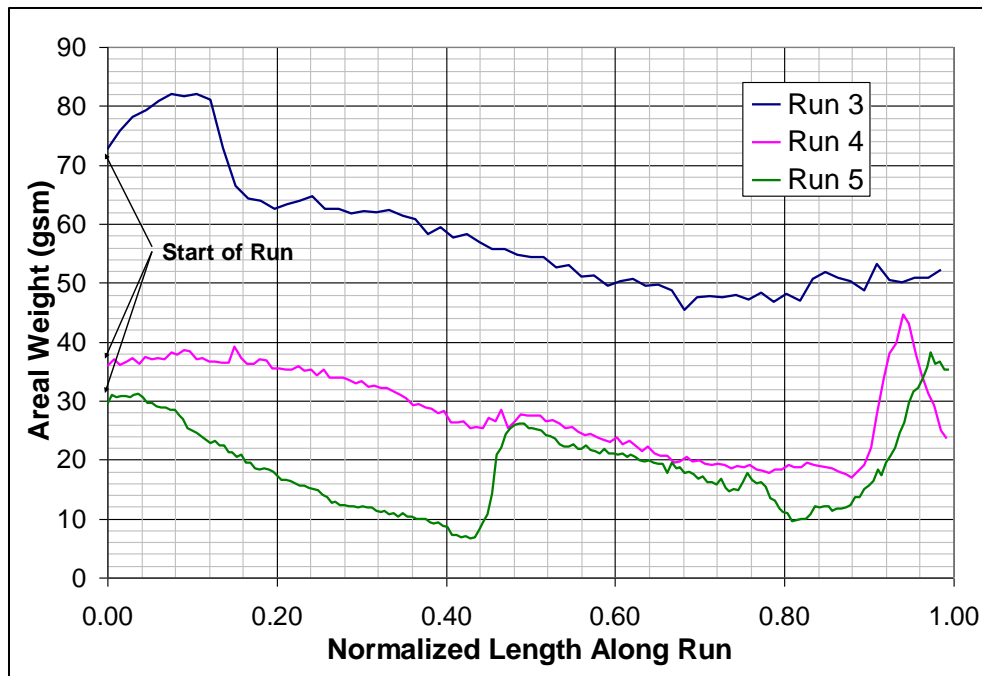
**Table 5.1 Properties of carbon fibers considered for blending study**

<b>Fiber</b>	<b>Tensile Strength (MPa)</b>	<b>Elastic Modulus (GPa)</b>	<b>Strain at Break (%)</b>	<b>Diameter (μm)</b>	<b>ρ (g/cm<sup>3</sup>)</b>
SGL [77]	4,000	227	1.6	7	1.8
AS4 [78]	4,480	231	1.8	7.1	1.79
IM7 [79]	5,480-5,570	276	1.8-1.9	5.2	1.78
Virgin T800S [80]	5,880	294	2.0	5	1.8
Recycled T800S [35]	5,543	256	1.9	5.2	1.8
Recycled T800S [14]	2,398	231	1.4	5.4	1.8



### **5.2.1 Procedure for using the wetlay process to make carbon fiber mats**

The wetlay process implemented at Southeast Nonwovens loaded 1.25cm (0.5in) chopped carbon fiber in a 1000L (250 gallon) mixing tank where viscosity modifiers and surfactants were added to the slurry to obtain ideal dispersion and flow properties before being pumped into the headbox of the inclined wire machine. The belt width of the machine is 0.8m (32in) but was limited to 0.6m (24in) so it could be passed through a convection oven with a 0.6m (24in) wide opening. To form the mat at the highest possible areal weight the belt speed was slowed down until the degree of fiber clumping created unacceptable uniformity, and then increased slightly to regain acceptable mat uniformity. When the mat reaches the level portion of the belt, it passes over additional water suction ports as well as under a binder application system. The binder solution is prepared in a dedicated mixing tank and then pumped into several faucet like applicators stretching across the width of the belt. Runs 1 and 2 using the AS4 and IM7 fibers were of poor quality and not characterized. The epoxy based binder used was with EPI-REZ 3520-WY-55 using 10wt% Epicure 8536-MV-60 as the hardener. Nalco 7768 was used as a dispersant.



**Figure 5.2 Wetlay process run uniformity. Run 3: 100% SGL, Run 4: 50% SGL/50% R-T800S, Run 5 100% RT800S**

Figure 2 shows variations in the areal weight of runs 3-5 along the length of the fabric. This variation can be a shortfall of the wetlay process if not closely monitored. The varying areal weight also meant each layer of fabric going into the RTM mold needed to be individually weighed to ensure near equal fiber loading from panel to panel. In all cases areal weight decreases with increasing duration indicating decreasing pumping speed from the mixing tank to the headbox as fabric is made. A constant level tank designed to keep constant pressure on the pump feeding the headbox was available, but was not used due to the small batch size of fiber used. The water level in a constant level tank is maintained by preparing additional slurry in a separate tank and then pumping the slurry from the extra tank to the constant level tank. Without the use of the leveling tank considerable variation in areal weight was measured as a result of different flow rates (Figure 2). The rise in areal weight of run 5 around 44% length is the result of slowing down the belt speed. As the water level dropped in the mixing tank the fiber flow into the headbox decreased resulting in a lighter

fabric mat. This lightness was noticed mid-run and the belt speed was decreased to increase the areal weight until increasing areal weight caused more clumping.

### **5.2.2 Resin Transfer Molding**

Rolls of fabric from runs three, four, and five were cut into 37cm x 37cm (14.5in x 14.5in) square sections and were stacked together to form a fiber preform targeting 1500g/m<sup>2</sup> areal weight. The fiber preform was then molded into a panel by Boeing Research and Technology in Seattle, WA using resin transfer molding and Hexcel RTM6™ resin (single component epoxy using Hexcel recommended 177°C (350°F) cure cycle). Two composite panels were made from runs 3 and from run 4. Southeast Nonwovens ran out of the epoxy binder after run 4 and a poly-vinyl alcohol (PVA) based binder was used for run 5 (100% recycled T800S). The PVA binder was washed out prior to molding to prevent undesirable interaction with the epoxy resin and cure cycle. One of the two fiber preforms made from run 5 lost its cohesion after rinsing out the PVA binder and could not be placed in the RTM mold. The second fiber preform was heated in an oven at 205°C to remove any volatiles from the PVA binder prior to molding.

### **5.2.3 Scanning Electron Microscopy**

Scanning electron microscopy (SEM) was used to characterize the fibers used in the blending study, fiber mats made using the wetlay process, and fracture surfaces from flexure samples. A JEOL 6400F Field Emission SEM along with Revolution 4 Pi Analysis for image acquisition was used. Three to four representative areas of each fiber sample were imaged at magnifications from 500X to 25,000X magnification. Of particular concern was oxidative damage such as pits and smoothed surface features of the R-T800S fibers resulting from the heat treatment. Similarly representative areas of fiber mat samples were captured at 20X to 500X magnification focusing on fiber architecture and contamination. Fracture surfaces were placed straight up on the sample holder; no tilt angle was needed to achieve a high depth of field image. Adobe Photoshop was used to make histogram and gamma adjustments on all images to make the images easier to see.

#### **5.2.4 Mechanical Testing**

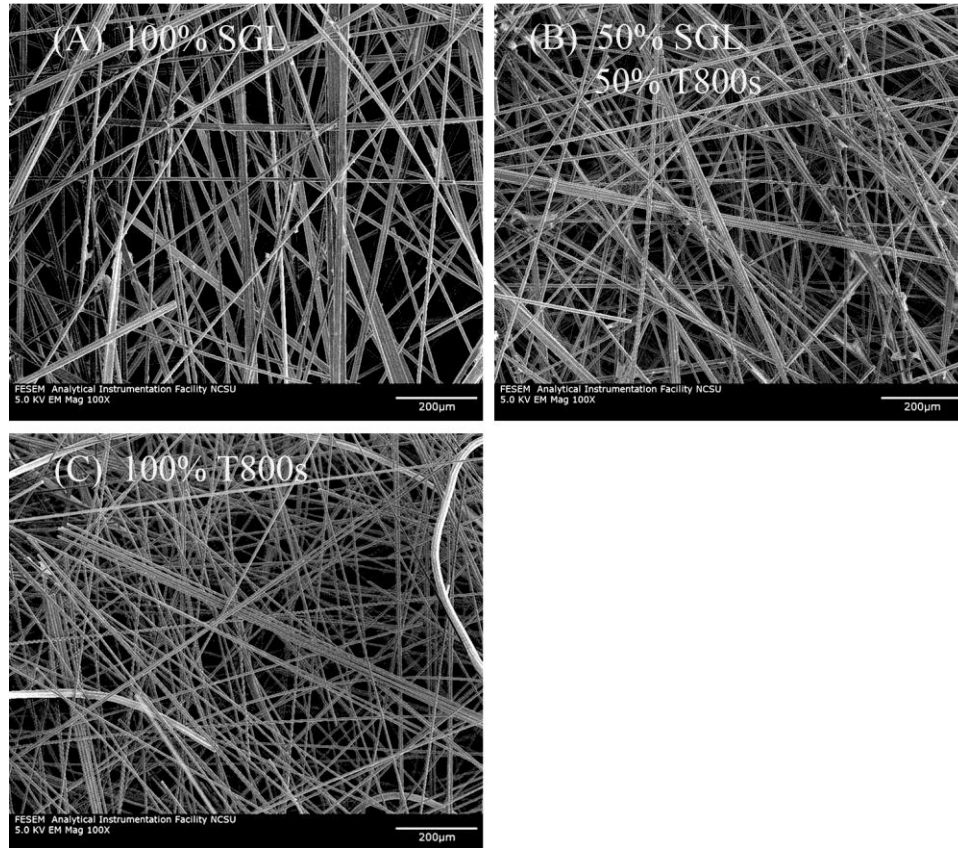
The panels made from RTM were cut, using a wet diamond saw, into test coupons for tensile, flexure, and compression testing. Boeing used internal test methods developed for high performance composites but also applicable to short fiber composites. The large coupon size and stringent fixturing requirements of the Boeing tests help ensure low standard deviation and high repeatability. Additionally, NC State and Boeing ran tests for tension, compression, and flexure according to ASTM standards for reinforced plastics. Tension and compression testing utilized an extensometer and flexure testing at NC State used a deflectionometer to measure coupon displacement. Since only one composite panel was made from run 5 material all mechanical testing for run 5 was conducted at Boeing. Fracture surfaces of flexure samples from NC State were observed using scanning electron microscopy. Tensile bars were of type I as defined in ASTM D 638 with an increased gauge width from 1.27cm (0.5in) to 1.9cm (0.75in) and an increased overall width from 1.9cm (0.75in) to 2.54cm (1.0in). Dogbone shaped samples with no tabs were used for compression testing and were dimensioned according to Figure 5 in ASTM D 695. Flexure tests were done in a 3 point bend configuration and a 16:1 span to depth ratio as indicated in ASTM D790.

### **5.3 Results & Discussion**

#### **5.3.1 Scanning Electron Microscopy**

Scanning electron microscopy was used to examine the construction of the mats at the filament level. Contamination, broken fibers, and adherence to the applied sizing was also studied. Figure 5.3 shows a section of each mat observed at 100X magnification. Varying levels of fiber density can be seen between fiber types. At such a small scale it is obvious the wetlay process cannot easily control microstructural features of the fiber preforms. In Figure 3A the filaments are well dispersed with only a few fibers stuck together. Figure 3B shows the 50/50 SGL/ R-T800S mat; the SGL fibers are visibly bigger. The filament bundles in Figure 5.3B are more prevalent and larger than in Figure 5.3A. Sizing is readily visible in

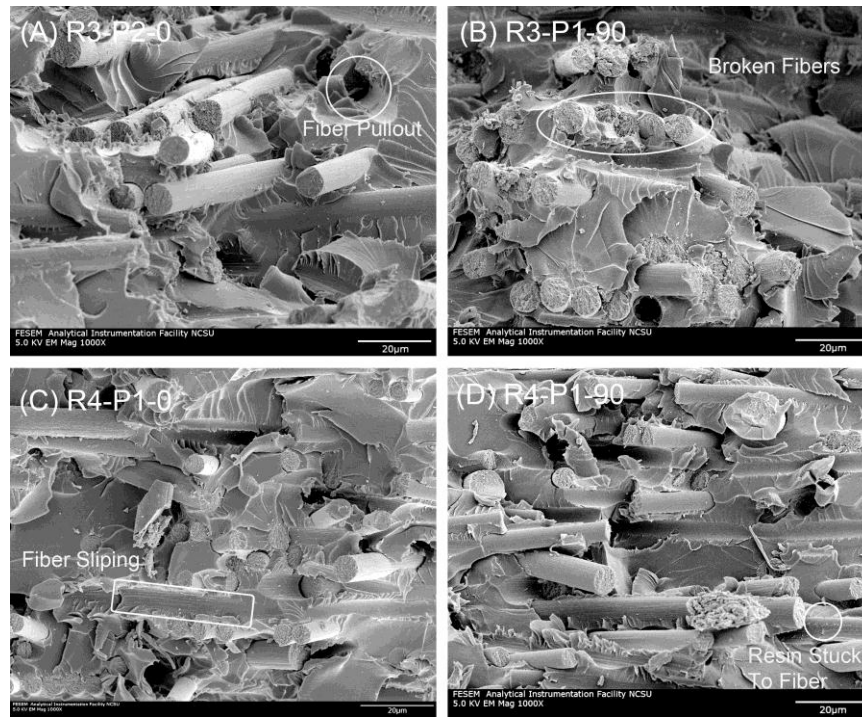
the right hand side of Figure 5.3B. The 100% T800S mat in Figure 5.3C looks much more closely packed than the mats in Figures 3A and 3B due to the smaller diameter of the R-T800S fibers. Many fiber ends are visible in Figure 5.3C which may indicate a weak R-T800S fiber that easily breaks during processing.



**Figure 5.3 Fiber architecture of wetlay mats**

SEM was also used to examine fracture surfaces from the samples broken by three point bending. The micrographs in Figure 5.4 are labeled with the run number of the wetlay process, panel number (1 or 2), and the direction of testing. Visible in all fracture surfaces are fiber pull out and evidence of the sample being bent. The fibers are slanted at a large angle as opposed to straight out of plane as they are for tensile failure; the hole the fibers are seated in is also oblong resulting in a

small gap along the long axis of the hole. The surface morphology of the SGL fibers versus the R-T800S fibers is also evident. The SGL fibers have striations running longitudinally while the R-T800S appears smooth at lower magnifications. The degree of fiber pullout and slipping is controlled by resin to fiber adhesion. Fibers shorter than the critical length will pull out (Figure 4A) or slide as opposed to breaking (Figure 4B), reducing the strength of the composite. Surface chemistry interactions and surface roughness control the interfacial shear strength of a composite. The trough, left by a sliding fiber, is smooth for R-T800S fibers or shows ridges that filled striations in SGL fibers (Figure 4C). Even broken fibers seem to have been partially pulled out leaving a relatively clean fiber surface. Small bits of resin are seen on both SGL and R-T800s fibers such as that circled in Figure 4D. The lack of clumps of resin such as that seen by Wong et al. [52, 55] suggests a diminished resin to fiber adhesion. Pimenta et al. suggested mechanical performance of RCFRPs could be improved by increasing resin to fiber adhesion, even though single fiber pull out tests indicated increased interfacial shear strength of RCF compared to VCF working with Toray T300 fibers [56].



**Figure 5.4. Fracture surfaces of flexure samples**

### 5.3.2 Mechanical Testing

Run 3 using 100% SGL fiber was generally the strongest material for all tests. Run 4 using 50% SGL and 50% recycled T800S fiber was always stiffer than run 3 due to the use of IM fibers, but increasing to 100% recycled T800S fibers did not always result in an increase of stiffness over run 4. Increased stiffness of run 4 materials over run 3 materials supports single filament testing results showing recycled fibers generally do not lose stiffness as a result of recycling [18, 37, 39].

Figure 5 is a combined plot showing tensile strength & modulus for Boeing and ASTM test methods. The ASTM test methods show larger variations in the data, but follow the trends in the Boeing test data. As expected blending R-T800S fiber as an IM fiber increases the elastic modulus of run 4 compared to just using SGL fiber which is a SM fiber. The 50/50 SGL/ R-T800S blend shows a slightly higher tensile strength than the 100% SGL fiber composite using Boeing tests while it is slightly lower using ASTM test procedures.

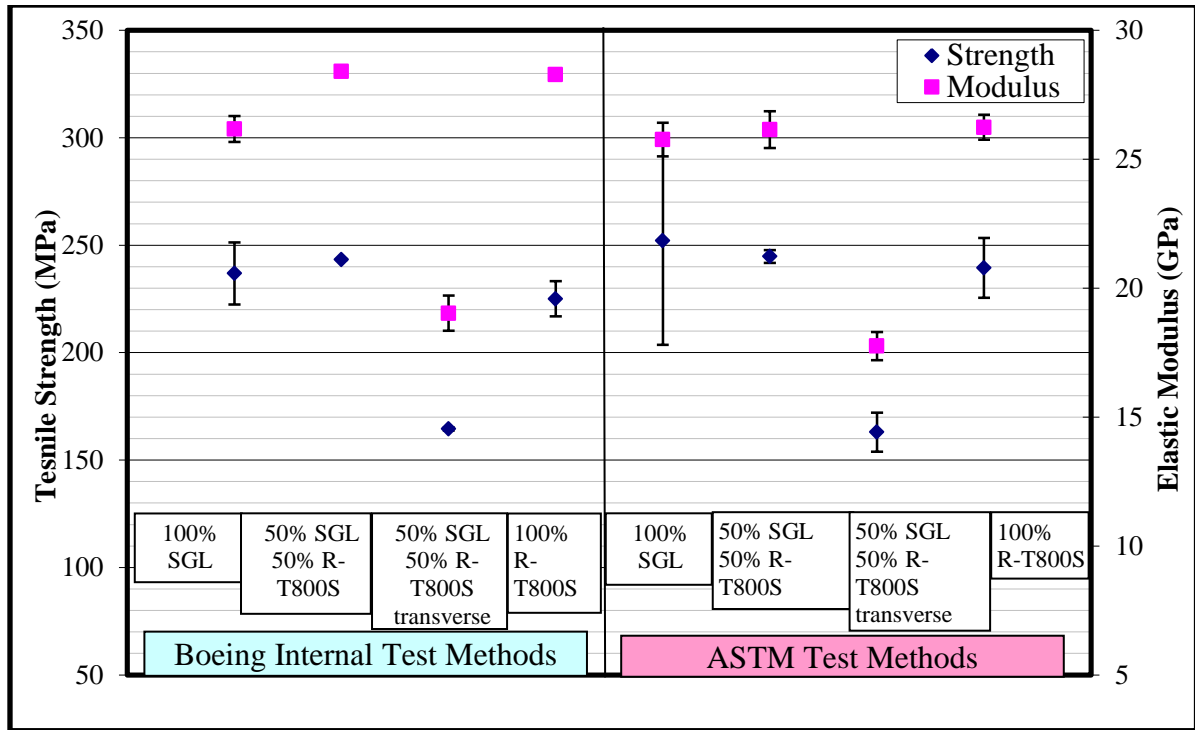
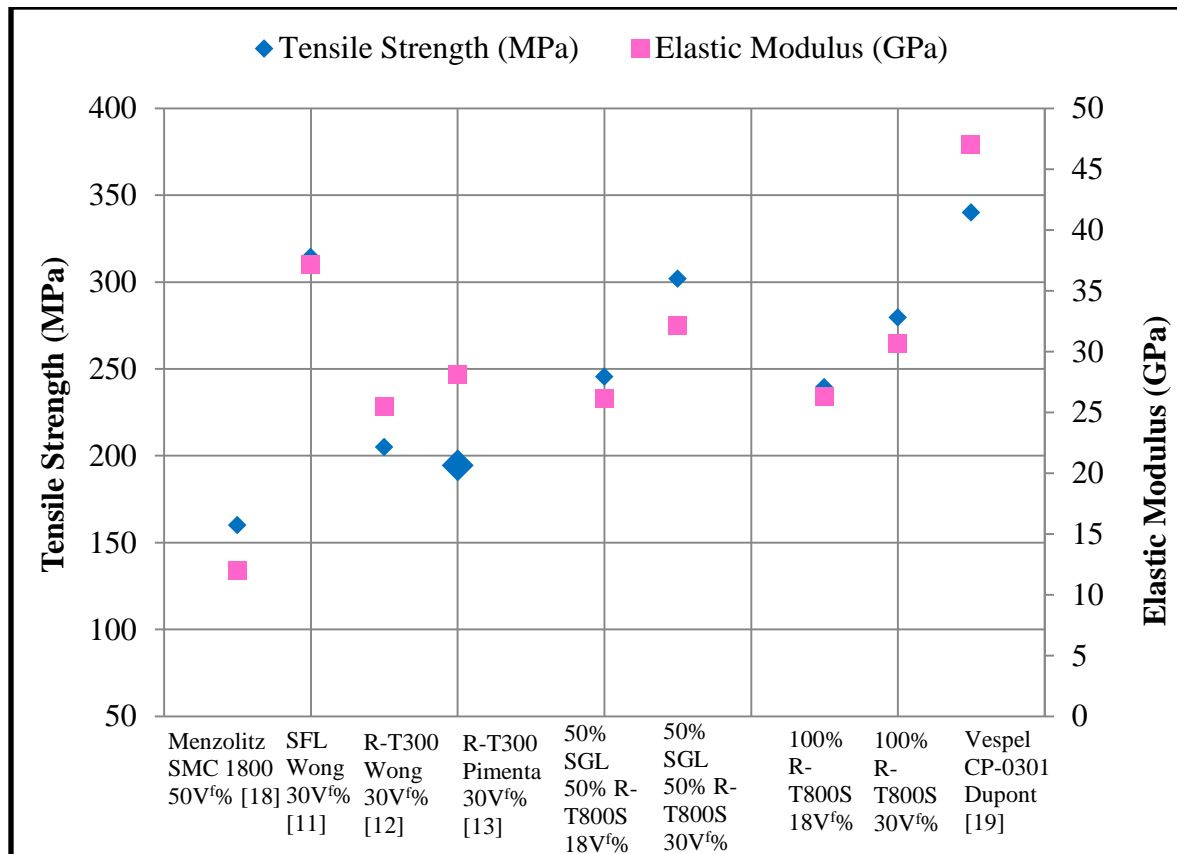


Figure 5.5. Tensile strength and modulus

To help put these test results into perspective Figure 5.6 shows tensile data from other researchers using recycled carbon fiber, but using different composite molding technologies. The tensile properties of runs 4 & 5 are presented in Figure 5.6 at the as tested 24 fiber volume percent and scaled to thirty percent fiber volume fraction ( $30V_f\%$ ) to match the fiber loading of Wong and Pimenta. Wong et al. prepared composites using recycled Toray T600 standard modulus fibers with fibers lengths of 8.5mm (short fiber laminate: SFL) [52] and Toray T300 fibers with lengths of 12mm before molding [55]. However under extreme molding pressures of 7MPa (1,000psi) for T600 and 14MPa for T300 the fibers fragment severely. In [55] only 30% of the fibers are longer than the critical reinforcement length. The T600 fibers had a tensile strength of 3.18GPa and an elastic modulus of 218GPa. The T300 fibers had a strength and modulus of 4.16GPa and 218GPa, respectively. Wong used the wetlay facilities at Technical Fibre Products (TFP) to convert the fibers into  $100\text{g/m}^2$  mats. The mats were stacked alternating with epoxy resin films. Laminates were molded

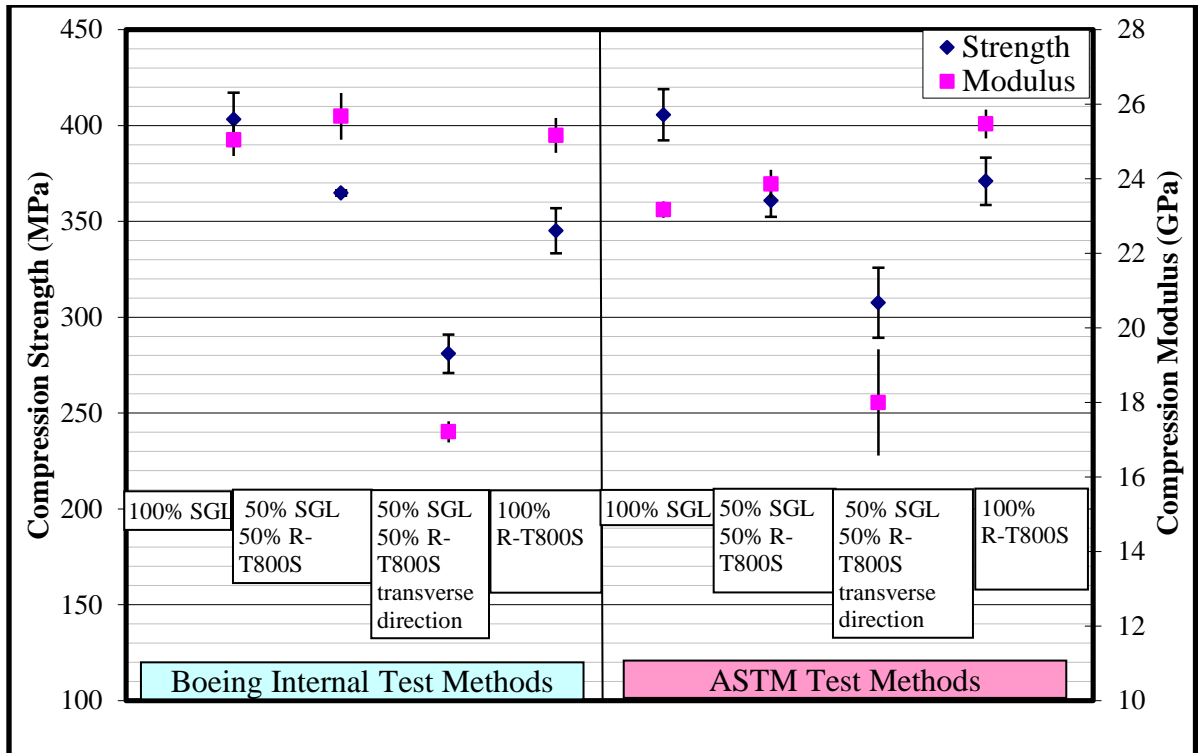


under compression and 120°C heating for 30 minutes. Wong [12] and Pimenta [56] used recycled Toray T300 fiber recovered from Milled Carbon's proprietary pyrolysis process. Recycled carbon fiber laminates were prepared by resin-film infusion of RCF mats produced by TFP in a near identical process utilized in [55]. Referring back to Table 5.1, the recycled T300 fibers are comparable to the virgin SGL fibers, while the T600s fibers are weaker than the SGL fibers but comparable in stiffness. Also from Table 1, the tensile strength and modulus of recycled T800S fibers is greater recycled T300 and T600 standard modulus fibers. Wong's short fiber reinforced laminate has similar strength and stiffness values to the 100% R-T800S composites. The Menzolit SMC 1800 is a glass fiber vinyl ester resin formulation with has similar tensile properties but better flexural properties compared to common SMCs used in the automotive industry (figure 9) [81]. Vespel CP-0301 is a Polyimide SMC reinforced with graphite and carbon fibers market for aerospace applications requiring high temperature stability and stiffness [82]. The 50/50 SGL/R-T800S blend with a fiber volume fraction of 0.24 has a higher strength and similar modulus to recently published rCFRP work in 2009 [12] and 2010 [13] as well as the 100% R-T800S composite. These observations may indicate the strength of short fiber composites is heavily dependent on fiber length whereas stiffness is less sensitive to fiber length. Scaling the strength and stiffness of the 50/50 SGL/R-T800s blend to 30 volume percent fiber results in a strength and stiffness exceeding [12] and [13]. Substantial reduction in fiber strength by a commercial pyrolysis recycling process presented in [14] may explain the lower strength of the scaled 50/50 SGL/R-T800s composite compared to the SFL laminate in [11]. Fibers in [11] were 60% aligned in the longitudinal direction which would explain the composites elastic modulus being higher than the 50/50 blend. As summarized by Figure 5.6, the composites made by the wetlay process compare quite favorably to other recycled carbon fiber composites and the performance of blended materials merits further investigation.



**Figure 5.6 Comparison of tensile test data to other recycled carbon fiber composite studies**

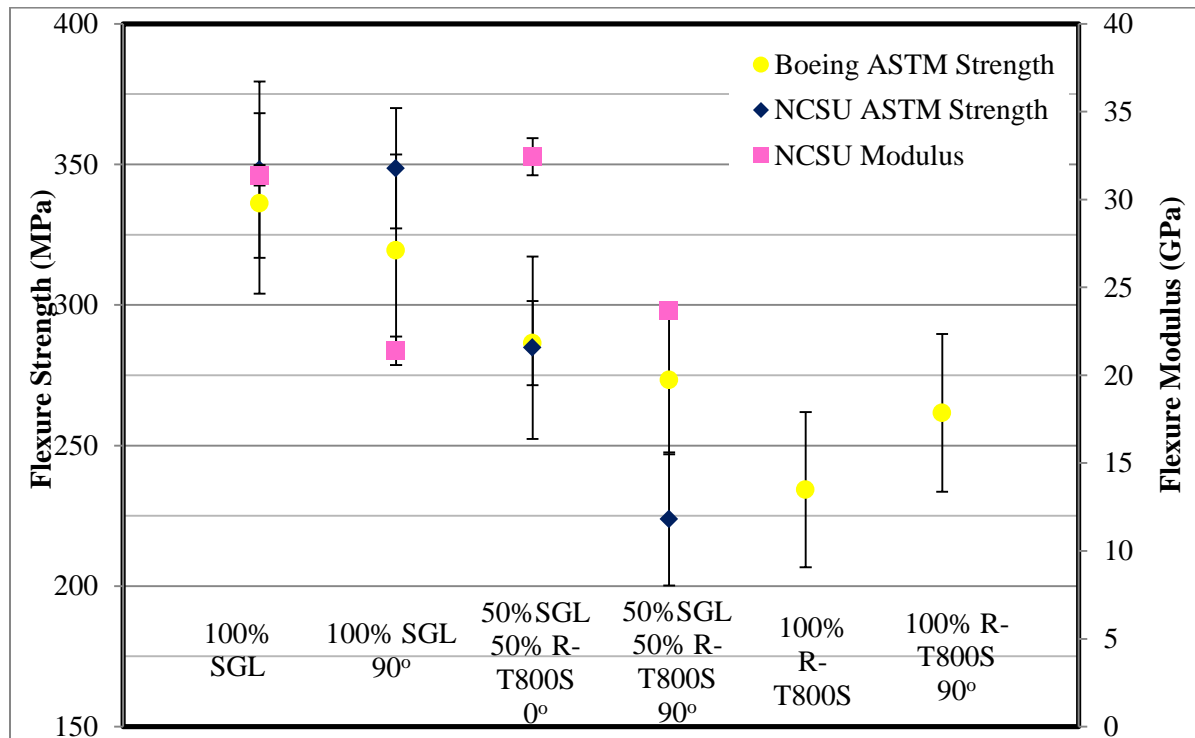
Compression testing showed more equal results between runs and less test variation than the tensile testing. Again the increased stiffness of runs 4 and 5 over run 3 can be attributed to IM fibers and the loss of stiffness measured by testing run 4 in the traverse direction indicates preferred fiber orientation in the  $0^\circ$  direction. According to the Euler equation, run 3 composite samples are less susceptible to buckling than composite samples from run 4 and 5 because of the larger diameter of SGL fibers versus R-T800S fibers [83]. Additionally, the Boeing Test Methods section of Figure 5.7 shows compression strength tracking with buckling resistance controlled by fiber diameter.



**Figure 5.7 Compression testing showing both Boeing and ASTM test method results**

Compressive strength can be extremely sensitive to fiber misalignment that allows for the formation of kink bands that represent shear yielding [60]. In Figure 5.7 the compression strength of the 100% R-T800S composite is significantly higher using the ASTM method than using the Boeing test method. ASTM D 695 shows a low compression modulus of the SGL fiber composite samples and larger increases in compression modulus from run 3 to run 4 and run 4 to run 5 compared to the Boeing test method. These trends suggest ASTM D 695 is more sensitive to the modulus of the fiber reinforcement than buckling or the formation of kink bands. The decrease in compression strength of run 4 compared to run 3 may be due to weaker recycled fibers or due to a greater proportion of out of plane fibers in the fiber preform made for run 4. Since tensile strength and flexure strength of run 4 is about equal to that of run 3; it would not seem likely that the recycled T800S fibers have a lower tensile strength than the SGL fibers.

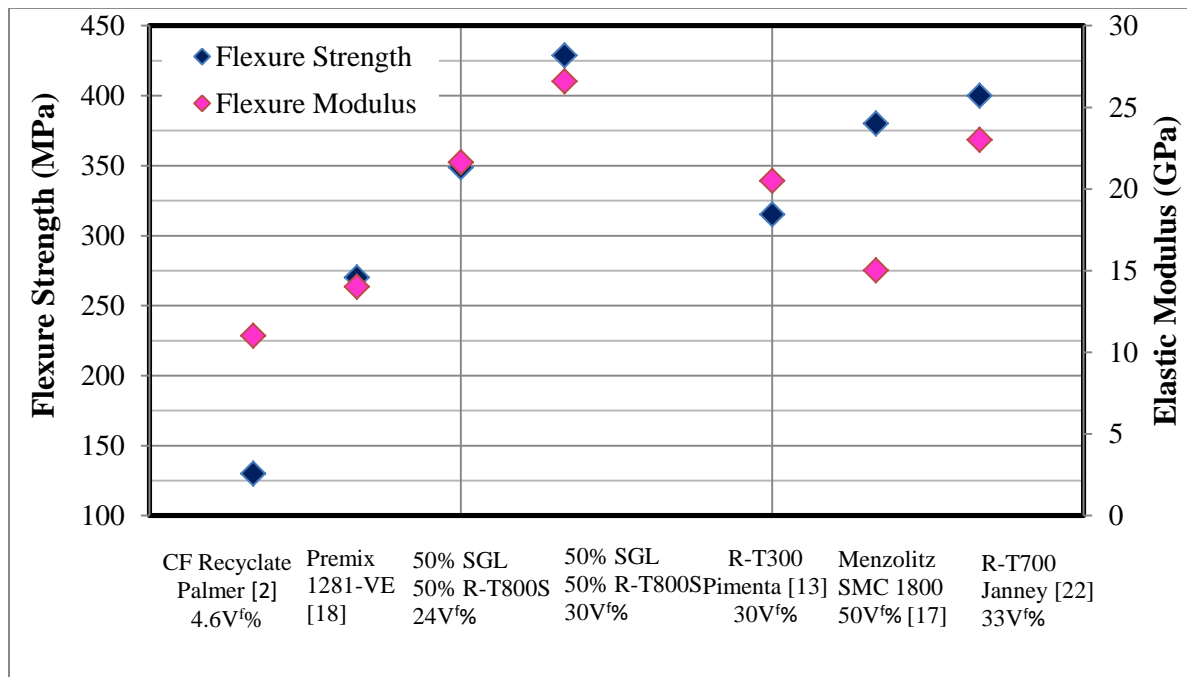
As shown in Figure 5.8 the flexure strength as determined by ASTM D790 using 3 point bending is very similar for run 3 using 100% SGL fiber and run 4 using a 50/50 mix of SGL/R-T800S fibers. Testing in the 90° direction shows a considerable loss in strength and stiffness compared to testing in the 0° direction for both run 3 and run 4. The decrease in strength along the 90° in run 4 is greater than that in run 3. Two reasons this happens may be a decrease in fiber orientation in run 4 compared to run 3 or more defects in the fabric preform that are dominant in the 90° direction but not the zero degree direction.



**Figure 5.8 Flexure test results (3 point bend configuration)**

Palmer et al. [23] report on recycling of CFRPs via comminution. In this study waste CFRP is granulated and separated into coarse and fine fiber as well as coarse and fine powder. The fine fibers were used to replace 20wt% of the glass fiber used in the manufacture of a commercially available SMC resulting in 4.6 volume percent of recycled carbon fiber. Figure 9 shows Palmer's SMC formulation to be slightly stiffer and a little bit

weaker than a typical 100% glass SMC used for structural applications. Palmer's SMC is also stronger and stiffer than the 50/50 SGL/ R-T800S blend at 4.6 fiber volume percent. The rCFRPs manufactured using the wetlay process and RTM were able to obtain significantly higher volume fraction carbon fiber than was attempted in Palmer's work. Comparing the RCF composites in figure 9, shows that the 50/50 SGL/ R-T800S blend has strength, stiffness, and weight savings superior to what is used in the automotive industry. Premix 1281-VE is a glass reinforced vinyl-ester SMC used for structural applications within the automotive industry [19]. Menzolit SMC 1800 has impressive flexural properties for a glass SMC but is considerably heavier at  $1.8\text{g/cm}^3$  than carbon fiber reinforced SMCs.



**Figure 5.9 Comparison of flexure properties to published recycled carbon fiber SMC study**

Janney [40, 73] reports on using recycled T700 fibers in Material Innovation Technologies (eMIT) 3-Dimensional Engineered Preform (3-DEP) [23, 84] process to create flat fiber preforms for compression molding. Long fibers (2.54cm) and low molding pressures (1.7MPa) are primarily responsible for the excellent mechanical performance

compared to other SMCs using RCF. Increasing fiber loading, for better strength and stiffness, in composites prepared from the wetlay process would be a promising counterpart to the 3-DEP process for the manufacture of recycled carbon fiber sheet molding compounds.

## 5.4 Conclusions

Recycled carbon fiber reinforced plastic composite materials have been made using the wetlay process to manufacture a fiber preform which was then resin transfer molded to form a composite test panel. The fiber preforms were randomly oriented but showed a slight preferential orientation in the machine direction taken as the 0° direction. Recycled Intermediate modulus carbon fibers were blended with virgin standard modulus carbon fibers to examine the effect of blending on mechanical properties. When recycled T800S fibers were blended with Sigrafil C30 fibers (SGL) the Tensile and Compression modulus of the blended composite increased over that of using 100% SGL fibers. Using recycled intermediate modulus carbon fibers had mixed effects on composite strength. Often, blending 50wt% intermediate modulus fibers decreased strength compared to virgin standard modulus fibers, but then using 100% recycled intermediate modulus fibers would increase the strength to between the 50/50 SGL/R-T800S blend and the 100% SGL composites. Strength and stiffness were severely reduced in the transverse direction under all loading conditions. The difference in flexure strength and modulus between the 100% SGL and 50/50 SGL/ R-T800S composites is negligible. For the 50/50 SGL/ R-T800S blend the flexure strength in the traverse direction dropped more sharply with respect to the machine direction than the 100% SGL sample did. However, the drop in flexure modulus for the 50/50 SGL/R-T800S blend is about the same as for the 100% SGL sample. Related work on creating a sheet molding compound by replacing a percentage of virgin glass fiber with recycled carbon fiber showed mechanical properties inferior to the simulated sheet molding compounds considered in this study. Studies in the UK have also used a papermaking process to create a recycled carbon fiber preform for purposes of molding a recycled carbon fiber composite. These studies were able to achieve 30 volume percent fiber loading and thus superior mechanical properties. The ASTM test methods for reinforced plastics were

conducted in parallel with Boeing test methods for composites to evaluate the suitability of the ASTM test procedures for short fiber composites. Testing was successful using ASTM procedures, but more work needs to be done to understand why Boeing and ASTM test methods do not produce the same trends.

## 6. Conclusions and Future Work

The work of IMST/NCSU presented in the preceding chapters details the most comprehensive analysis, from an independent source, on recycled carbon fiber. As evident from the introduction substantial contributions to carbon fiber recycling literature comes from Imperial College London and The University of Nottingham, but ISMT/NCSU has specialized in fiber analysis and thus is able to present a history of carbon fiber recycling encompassing multiple materials and processes.

The most basic conclusion stemming from this work is that the morphological, surface chemistry and mechanical properties of recycled carbon fibers make them suitable for reuse in load bearing composite structures. Several trends are evident from fiber testing. SEM shows differences in fiber morphology based on material feedstock such as the difference between T300 fiber recycled from cured and uncured trim scrap. Standard modulus fibers seem to be ‘easier’ to recycle as their reduction in mechanical properties is less than that of intermediate modulus fibers. Examining fiber strength dependence on gauge length is a valuable analysis when assessing how or where to use recycled carbon fiber. Quite commonly fiber strength at short gauge lengths such as at 6mm showed fiber strength on par with virgin fiber. However at longer gauge lengths the strength of recycled carbon fibers dropped more rapidly than predicted based on testing of virgin carbon fiber. Intermediate modulus fibers are especially likely to display this behavior. The elastic modulus of recycled carbon fibers is generally the same or higher than that of virgin fibers and does not decrease with increasing gauge length indicating applications prioritizing stiffness over strength may be immediate avenues for the reuse of recycled carbon fiber.

The wetlay and sheet molding work has some notable firsts. It is the first time, in the United States, that a conventional wetlay process has been used to process recycled carbon fiber into sheets uniform enough for composites molding, the first time carbon fibers recycled in a production scale facility have been used in a composite, the first time resin transfer molding has been used to make a sheet molding compound containing recycled carbon fiber, and it is also the first time recycled carbon fiber has been blended with virgin



carbon fiber to study the mechanical performance of a composite as a function of varying recycled carbon fiber content. The comparison of the SMCs described in this thesis to other SMCs using recycled carbon fiber show that there is a substantial benefit to using resin transfer molding over compression molding. Through optimization of the wetlay process and using recycled carbon fibers with only 10-20% reduction in strength as seen from pilot scale recycling processes, resin transfer molding offers the opportunity to make recycled carbon fiber sheet molding compounds that are competitive with virgin carbon fiber sheet molding compounds currently used by the aerospace industry.

Testing of recycled carbon fibers indicated they are suitable for reuse. However finding the right application and processing method for the reuse of recycled carbon fibers is tricky. Processes that seem particularly well suited for recycled carbon fiber are extrusion compounding followed by injection molding and slurry based processes such as 3-DEP and variations of the wetlay process. Composites using short fiber lengths will see virtually no performance impact by using recycled carbon fiber. In conclusion this thesis investigates the properties of recycled carbon fibers, explains the analysis based on fiber type and feedstock to the recycling process, shows the most recent efforts to make recycled carbon fiber composites and uses this knowledge to suggest paths for future work in carbon fiber recycling.

Future work will complement the existing data on sheet molding processes by: examining fiber length distribution, before & after the wetlay process, and after the resin transfer molding, measuring the tensile strength of the fibers used, and check to see if the composite mechanical properties models developed at Imperial College London work equally well for composites made by resin transfer molding as they do for composites made using compression molding. Continuing with the wetlay theme efforts to make aligned fiber preforms, denser preforms, and to control the level of filamentization are of great value. Considering that electron microscopy gives no or misleading evidence of microstructural fiber damage measured by single filament tensile testing suggests the need to further understand what nano- & micro-structural features of carbon fiber are responsible for strength and stiffness and how can they be altered independently.

## 7. References

1. Callister WD, 1940-. Materials science and engineering : An introduction. David G. Rethwisch. John Wiley & SonsHoboken, NJ: ; 2010. .
2. Polyacrylonitrile (PAN) carbon fibers industrial capability assessment. Department of Defense; 2005 October.
3. Johnson DJ. Structure-property relationships in carbon fibres. J Phys D 1987 20; (3):286.
4. Reed-Hill RE, Abbaschian R. Chapter 22 fracture mechanics. In: Jonathan Plant, Mary Thomas, editors. PhysicalMetallurgy principals. 3rd ed. Bostonm, Ma: PWS Publishing Company; 1994. .
5. Fitzer E, Heine M. Carbon fiber manufacture and surface treatment. In: A. R. Bunsell, editor. Fiber reinforcements for composite materials. Amsterdam: Elsevier; 1988. Chapter 2.
6. Abhiraman AS. Precursor structure - fiber property relationships in polyacrylonitrile-based carbon fibers. ; 1992.
7. Gupta AK, Paliwal DK, Bajaj P. Acrylic precursors for carbon fibers. 1991 31; (1):89.
8. Abhiraman AS. Precursor structure-fiber property relationships in polyacrylonitrile-based carbon fibers. Georgia: ; 1990 07:undefined; Compiled and Distributed by the NTIS, U.S. Department of Commerce. It contains copyrighted material. All rights reserved. 2008.
9. Dieter GE. Fracture mechanics. In: Michael B. Bever, Stephen M. Copely, M. E. Shank, Charles A. Wert, Garth L. Wilkes, editors. Mechanical metallurgy. Si Metric ed. London: McGraw Hill Book Company; 1988. .
10. Kobayashi H. Toray's advanced materials: Innovation by chemistry. Toray Advanced Materials Symposium; 2006 9/27.
11. Reynolds WN, Sharp JV. Crystal shear limit to carbon fibre strength. Carbon 1974 12; (2):103.
12. Silva JLG, Johnson DJ. Flexure studies of carbon fibres. Journal of Materials Science 1984 19; (10):3201.
13. Jing M, Wang C, Zhu B, Wang Y, Gao X, Chen W. Effects of preoxidation and carbonization technologies on tensile strength of PAN-based carbon fiber. Journal of Applied Polymer Science 2008 108; (2):1259-64.

14. Triaxial Weaving [Internet]: Tyler, Tim [cited 2011 . Available from:  
<http://hexdome.com/weaving/triaxial/index.php>.
15. 3Tex Technologies [Internet]: 3Tex, Inc; c2007 [cited 2011 . Available from:  
<http://www.3tex.com/node/8>.
16. Mohamed M. Large scale joint fabrication using 3-D fabric preforms, sandwich core structure and VARTM processing. SAMPE Journal 2008;44(55).
17. Davidson J, Roy P, inventors. Recycling carbon fibre. Milled Carbon Limited, editor. Great Britain patent WO 2009/090264. 2009 July 23.
18. Pickering SJ. Recycling technologies for thermoset composite materials - current status. Composites Part A-Applied Science and Manufacturing 2006 37; (8):1206-15.
19. Jan-Michael Gosau. State-of-the-art 2nd generation aircraft composites. SAMPE 2009 technical conference proceedings: Changing times. new opportunities. are you ready?; May 18-21, 2009; Baltimore, MD: Soc. for the Advancement of Material and Process Engineering.
20. Jan-Michael Gosau, Tyler F. Wesley and Ronald E. Allred. Integrated composite recycling process. 38th SAMPE fall technical conference: Global advances in materials and process engineering; November 6-9, 2006; Dallas, TX, United states: Soc. for the Advancement of Material and Process Engineering.
21. Perrin D, Leroy E, Clerc L, Bergeret A, Lopez-Cuesta JM. Treatment of SMC composite waste for recycling as reinforcing fillers in thermoplastics. Macromolecular Symposia 2005 221;:227-36.
22. Perrin D, Clerc L, Leroy E, Lopez-Cuesta J-, Bergeret A. Optimizing a recycling process of SMC composite waste. Waste Management 2008 28; (3):541-8.
23. Palmer J, Ghita OR, Savage L, Evans KE. Successful closed-loop recycling of thermoset composites. Composites Part A-Applied Science and Manufacturing 2009 40; (4):490-8.
24. The Japan Carbon Fiber Manufacturing Association: FAQ [Internet]: The Japan Carbon Fiber Manufacturing Association; c2011 [cited 2011 3/14]. Available from:  
<http://www.carbonfiber.gr.jp/english/index.html>.
25. About Us [Internet]: Recycled Carbon Fiber, Ltd.; c2010 [cited 2011 . Available from:  
<http://www.recycledcarbonfibre.com/about-recycled-carbon-fibre.html>.

26. William L. Carberry. An update on work with recycled carbon fibre for aircraft components. 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International, Intertech Pira.
27. Roland Thevenin. Carbon fibre in aerospace: We know about the present... but what about the future? 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International, Intertech Pira.
28. Pete E. George. Perspective on carbon fiber recycling from a major end user. Carbon fibre recycling and reuse: Developing a supply chain for waste CFRP; November 3-4, 2009; Hamburg, Germany: Pira International, Intertech Pira.
29. R. E. Allred, J. M. Gosau and J. M. Shoemaker. Recycling process for carbon/epoxy composites. 46th international SAMPE symposium and exhibition 2001: A materials and processes odyssey; May 6-10, 2001; Long Beach, CA, United states: Soc. for the Advancement of Material and Process Engineering.
30. Brian E. Allen, Myles L. Connor, Joseph P. Heil, Jerome J. Cuomo, Pete E. George and William L. Carberry. Recycled carbon fiber analysis: Morphological and chemical characterization. Proceedings of the 38th SAMPE international technical conference; November 6-9; SAMPE.
31. Myles L. Connor, Joseph P. Heil, Jerome J. Cuomo, Pete E. George and William L. Carberry. Recycled carbon fiber analysis: Mechanical properties. 38th SAMPE fall technical conference: Global advances in materials and process engineering; November 6-9, 2006; Dallas, TX: Soc. for the Advancement of Material and Process Engineering.
32. Pete E. George, William L. Carberry, Myles L. Connor and Brian E. Allen. Recycled carbon fiber performance in epoxy and polycarbonate matrices. Composites innovation; October 4-5, 2007; Barcelona, Spain: .
33. Jan-Michael Gosau. Recovering carbon fibre and more from scrap composite material. Carbon fibre recycling & reuse developing a supply chain for waste CFRP; November 3-4, 2009; Hamburg, Germany: Pira International/IntertechPira.
34. Giacinto Cornacchia, Sergio Galvagno, Sabrina Portofino, et al. Carbon fiber recovery from waste composites: An integrated approach for a commercially successful recycling operation. SAMPE 2009 technical conference proceedings: Changing times. new opportunities. are you ready?; May 18-21, 2009; Baltimore, MD, United states: Soc. for the Advancement of Material and Process Engineering.
35. Joseph P. Heil, Michael J. Hall, Davis R. Litzenberger, et al. A comparison of chemical, morphological, and mechanical properties of various recycled carbon fibers. SAMPE 2009 technical conference proceedings: Changing times. new opportunities. are you

ready?; May 18-21, 2009; Baltimore, MD, United states: Soc. for the Advancement of Material and Process Engineering.

36. McConnell VP. Launching the carbon fibre recycling industry. *Reinforced Plastics* 2010 54; (2):33-7.
37. Joseph P. Heil, Davis R. Litzenberger and Jerome J. Cuomo. A comparison of chemical, morphological, and mechanical properties of carbon fibers recovered from commercial recycling facilities. *SAMPE 2010 technical conference proceedings new materials and processes for a new economy*; May 17-20, 2010; Seattle, Wa: Soc. for the Advancement of Material and Process Engineering.
38. Soraia Pimenta. Mechanical performance of a recycled composite has been measured to be similar to that of an aerospace-grade woven composite. *13th annual global outlook for carbon fibre*; September 29-30, 2010; Valencia, Spain: Pira International/IntertechPira.
39. Silvestre Pinho. How the microstructure of recycled composites can be tailored during recycling. *13th annual global outlook for carbon fibre*; September 29-30, 2010; Valencia, Spain: Pira International/IntertechPira.
40. Mark A. Janney, W. L. Newell, Ervin Geiger, Neal Baitcher and Tod Gunder. Manufacturing complex geometry composites with recycled carbon fiber. *Spring symposium conference proceedings: Changing times. new opportunities. are you prepared?*; May 18-21, 2009; Baltimore, MD, United states: Soc. for the Advancement of Material and Process Engineering.
41. William L. Carberry. Aerospace's role in the development of the recycled carbon fibre supply chain. *Carbon fibre recycling and reuse: Developing a supply chain for waste CFRP*; November 3-4, 2009; Hamburg, Germany: Pira International/IntertechPira.
42. William L. Carberry. Aircraft & composite recycling. *38th SAMPE fall technical conference: Global advances in materials and process engineering*; November 8, 2006; Dallas, Tx: Soc. for the Advancement of Material and Process Engineering.
43. Jiang G, Pickering SJ, Walker GS, Bowering N, Wong KH, Rudd CD. Soft ionisation analysis of evolved gas for oxidative decomposition of an epoxy resin/carbon fibre composite. *Thermochimica Acta* 2007 454; (2):109-15.
44. Jiang G, Pickering SJ, Lester EH, Turner TA, Wong KH, Warrior NA. Characterisation of carbon fibres recycled from carbon fibre/epoxy resin composites using supercritical n-propanol. *Composites Science and Technology* 2009 69; (2):192-8.

45. Hyde JR, Lester E, Kingman S, Pickering S, Wong KH. Supercritical propanol, a possible route to composite carbon fibre recovery: A viability study. *Composites Part A- Applied Science and Manufacturing* 2006 37; (11):2171-5.
46. Loppinet-Serani A, Aymonier C, Cansell F. Supercritical water for environmental technologies. *Journal of Chemical Technology & Biotechnology* 2010 85; (5):583-9.
47. Mormann W, Frank P. Supercritical ammonia for recycling of thermoset polymers. *Macromolecular Symposia* 2006 242;:165-73.
48. Piñero-Hernanz R, García-Serna J, Dodds C, Hyde J, Poliakoff M, Cocero MJ, Kingman S, Pickering SJ, Lester E. Chemical recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions. *The Journal of Supercritical Fluids* 2008 46; (1):83-92.
49. Pinero-Hernanz R, Dodds C, Hyde J, Garcia-Serna J, Poliakoff M, Lester E, Cocero MJ, Kingman S, Pickering S, Wong KH. Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water. *Composites Part A: Applied Science and Manufacturing* 2008 39; (3):454-61.
50. Marsh G. Carbon recycling: A soluble problem. *Reinforced Plast* 2009 53; (4):22-7.
51. S. J. Pickering, T. A. Turner and N. A. Warrior. Moulding compound development using recycled carbon fibres. 38th SAMPE fall technical conference: Global advances in materials and process engineering; November 6-9, 2006; Dallas, TX, United states: Soc. for the Advancement of Material and Process Engineering.
52. K. H. Wong, S. J. Pickering, T. A. Turner and N. A. Warrior. Preliminary feasibility study of reinforcing potential of recycled carbon fibre for flame-retardant grade epoxy composite. *Composites innovation* 2007- improved sustainability and environmental performance; 2007; Barcelona, Spain: .
53. Harper LT, Turner TA, Warrior NA, Rudd CD. Characterisation of random carbon fibre composites from a directed fibre preforming process: The effect of tow filamentisation. *Composites Part A: Applied Science and Manufacturing* 2007 38; (3):755-70.
54. Harper LT, Turner TA, Warrior NA, Dahl JS, Rudd CD. Characterisation of random carbon fibre composites from a directed fibre preforming process: Analysis of microstructural parameters. *Composites Part A: Applied Science and Manufacturing* 2006 37; (11):2136-47.
55. Kok H. Wong, Stephen J. Pickering, Thomas A. Turner and Nicholas A. Warrior. Compression moulding of a recycled carbon fibre reinforced epoxy composite. SAMPE '09 spring symposium conference proceedings; May 18-21, 2009; Baltimore, MD, United states: Soc. for the Advancement of Material and Process Engineering.

56. Pimenta S, Pinho ST, Robinson P, Wong KH, Pickering SJ. Mechanical analysis and toughening mechanisms of a multiphase recycled CFRP. *Composites Science and Technology* 2010 70; (12):1713-25.
57. Soraia Pimenta, Silvestre Pinho and P. Robinson. Closing the loop: Mechanical analysis and modeling of a multiscale recycled composite. 14th european conference on composite materials; June 7-10, 2010; .
58. Soraia Pimenta. Mechanical analysis of recycled CFRP. Carbon fibre recycling and reuse: Developing a supply chain for waste CFRP; November 3-4, 2009; Hamburg, Germany: Pira International/IntertechPira.
59. Pimenta S, Gutkin R, Pinho ST, Robinson P. A micromechanical model for kink-band formation: Part I - experimental study and numerical modelling. *Composites Sci Technol* 2009 69; (7-8):948-55.
60. Pinho ST, Iannucci L, Robinson P. Physically-based failure models and criteria for laminated fibre-reinforced composites with emphasis on fibre kinking: Part I: Development. *Composites Part A: Applied Science and Manufacturing* 2006 37; (1):63-73.
61. John Marcheschi. Recycled carbon fibre plant design & build solution. 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International/Intertech Pira.
62. Thomas Hunter. Challenges in engaging upstream users in the recycling process. 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International/IntertechPira.
63. Spirit Aerosystems: Design/Build - Fuselage [Internet] [cited 2011 2/24]. Available from: <http://www.spiritaero.com/Content.aspx?id=2551>.
64. Kevin Gaw and Pete E. George. Use of recycled aerospace grade carbon fibers in thermoplastic articles. SAMPE 2010 technical conference proceedings: New materials and processes for a new economy; May 17-20, 2010; Seattle, Wa: Soc. for the Advancement of Material and Process Engineering.
65. Thomas A. Turner, Stephen J. Pickering and Nicholas A. Warrior. Development of high value composite materials using recycled carbon fibre. SAMPE '09 spring symposium conference proceedings; May 18-21, 2009; Baltimore, MD, United states: Soc. for the Advancement of Material and Process Engineering.

66. Robson S, Goodhead TC. A process for incorporating automotive shredder residue into thermoplastic mouldings. *Journal of Materials Processing Technology* 2003 139; (1):327-31.
67. Groning M, Hakkarainen M, Albertsson AC. Recycling of glass fibre reinforced phenolic prepreg waste. part 1. recovery and reuse of glass fibres in PP and PA6. *Polymers & Polymer Composites* 2004 12; (6):491-500.
68. Stephen J. Pickering. Alignment of recycled carbon fibre for high volume fraction composites. 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International/IntertechPira.
69. Netravali AN, Henstenburg RB, Phoenix SL, Schwartz P. Interfacial shear strength studies using the single-filament-composite test. I: Experiments on graphite fibers in epoxy. *Polymer Composites* 1989 10; (4):226-41.
70. Drzal LT, Rich MJ, Lloyd PF. Adhesion of graphite fibers to epoxy matrices: I. the role of fiber surface treatment. *The Journal of Adhesion* 1983 16; (1):1-30.
71. Park S, Kim M. Effect of acidic anode treatment on carbon fibers for increasing fiber-matrix adhesion and its relationship to interlaminar shear strength of composites. *Journal of Materials Science* 2000 35; (8):1901-5.
72. Deakin S. Required packaging & material standards for carbon composite waste deliveries to recycled carbon fibre ltd. Cannon Buisness Park, Coseley, Dudley, Westmidlands, WV14 8XR, UK: ; 2009.
73. Mark A. Janney and David P. Haack. Fabrication of net-shape, chopped fiber preforms by the 3-DEP process. *Carbon fiber* 2007; December 5-7, 2007; Yarmouth, ME: CompositesWorld.
74. Goda K, Park JM, Netravali AN. New theory to obtain weibull fibre strength parameters from a single-fibre composite test. *J Mater Sci* 1995 30; (10):2722-8.
75. Mark James. Recycled nonwoven materials for the future: From fuel cells to aerospace. 13th annual global outlook for carbon fibre; September 29-30, 2010; Valencia, Spain: Pira International/IntertechPira.
76. Weeks GP, inventor. Composites made from wet formed blends of glass and thermoplastic fibers. E.I. DuPont de Nemours and Company, editor. Delaware/USA patent 5,4095,73. 1995 April 25 1993 December 28.



77. SGL Carbon Fibers Ltd. Sigrafil C the PAN-based carbon fiber. Gardena, CA: SGL Group The Carbon Company; 2010  
03/2010:[http://www.sglgroup.com/export/sites/sglcarbon/\\_common/downloads/products/product-groups/cf/carbon-fibers-for-braided-packings-and-gaskets/SIGRAFIL\\_C\\_PAN\\_Based\\_Carbon\\_Fiber\\_e.pdf](http://www.sglgroup.com/export/sites/sglcarbon/_common/downloads/products/product-groups/cf/carbon-fibers-for-braided-packings-and-gaskets/SIGRAFIL_C_PAN_Based_Carbon_Fiber_e.pdf).
78. HexTow AS4 carbon fiber product data. Stamford, Connecticut: Hexcel Corporation; 2010.
79. HexTow IM7 carbon fiber product data. Stamford, Connecticut: Hexcel Corporation; 2010.
80. TORAYCA. T800S data sheet. Santa Anna, California: Toray Carbon Fibers America, Inc. Report nr CFA-019.
81. Premi-glass 1281-47VE structural sheet molding compound technical data sheet. North Kingsville, OH: Premix; 2010 May  
19:<http://www.premix.com/datasheets/05Automotive/Premi-Glas%201281-47VE%20Structural%20SMC.pdf>.
82. Typical properties vespel sheet molding compound CP-0301 & 0801. Newark, Delaware: Dupont; 2003. Report nr VCP10301-053003:[http://www2.dupont.com/Vespel/en\\_US/assets/downloads/vespel\\_cp/cp0301.pdf](http://www2.dupont.com/Vespel/en_US/assets/downloads/vespel_cp/cp0301.pdf).
83. Hull D. An introduction to composite materials. 2nd ed. T. W. Clyne. Cambridge University PressCambridge England ; New York: ; 1996. .
84. Mark A. Janney, Ervin Geiger and Neal Baitcher. Fabrication of chopped fiber preforms by the 3-DEP process. Composites & polycon 2007; October 17-19, 2007; American Composites Manufacturers Association.

