ABSTRACT

ALLEN, BRIAN EDWARD. Characterization of Reclaimed Carbon Fibers and their Integration into New Thermoset Polymer Matrices via Existing Composite Fabrication Techniques. (Under the direction of Dr. Jerome J. Cuomo.)

The carbon fiber reinforced plastics (CFRP) industry is currently growing at a substantial rate. As this growth continues, so does waste generated both from manufacturing scrap and end-of-life (EOL) composites. Recognizing the abundance of composite scrap, recycling companies have generated technologies to recover the carbon fibers (CFs). This research determined if recycled carbon fibers (RCFs) retain their inherent value compared to virgin carbon fibers. Once proven, the fibers were reintroduced into thermoset polymer matrices using existing composite fabrication techniques.

This research first characterized recovered carbon fibers from cured Air Force grade composites. The CFRP originally contained Huntsman 8606 epoxy resin and unknown CFs. The composite was exposed to four proprietary reclamation techniques determining which treatment yielded CFs with the best surface and mechanical properties compared to virgin AS4 carbon fiber. Depending on the treatment, single fiber tensile testing (SFTT) proved the RCFs retained anywhere from 35% - 74% of the virgin fiber's ultimate tensile strength. The 35% retention is quite poor, indicating the reclamation treatment requires optimization. However, the 74% strength retention is quite promising, revealing potential for the RCFs to function suitably when reintroduced into composite components.

Scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) revealed the RCFs and the virgin control fiber had similar surface properties. SEM micrographs revealed the reclamation techniques did not damage the fibers, yet in some cases, 100% of the resin was not completely removed. Deconvolution of the C 1s peak,

derived from the XPS data, revealed the RCFs and the virgin fiber had similar surface functionalities. This data is extremely promising for fiber to resin adhesion.

The RCFs were next used as the reinforcement material in composite panels. Thermoset polymers, including epoxy, vinyl ester, and phenolic resins, were used as the matrix materials. The composite fabrication techniques included vacuum assisted resin transfer molding (VARTM), bulk molding compounds (BMCs), and compression molding. Recycled carbon fiber reinforced plastics (R-CFRPs) were successfully constructed and underwent tensile, flexure, compression, and interlaminar shear strength testing to determine their mechanical properties.

Overall, the R-CFRPs had inferior mechanical properties compared to the virgin reinforced composites. In some cases, a considerable decrease in strength was seen (as low as 87% decrease in tensile strength). The fibers most likely did not adhere to the resin as well as the control fiber. However, with respect to interlaminar shear strength, the R-CFRPs compared quite favorably to the virgin reinforced composites. The IM7 virgin fibers used to fabricate virgin CFRPs contained sizing which helped promote adhesion to the thermoset resin used. This sizing enhanced the fiber/resin adhesion, thus outperforming the R-CFRPs which contained RCFs without sizing. In addition, the IM7 fiber was a higher modulus fiber compared to the reclaimed fibers.

A BMC was also formulated using milled RCFs and a phenolic resin. The BMC charge was compression molded into a 3-D circuit breaker panel cover. This showed proof of concept that reclaimed carbon fibers could be integrated with a phenolic resin producing an actual composite part.

The Boeing Company also provided recycled carbon fibers for analysis that were derived from manufacturing scrap. The recycled and virgin fibers were characterized using SEM, XPS, and SFTT. The fibers had extremely clean surfaces compared to RCFs derived from cured composite material. Also, the fibers retained 50% - 100% of their tensile strength. Recycled fibers derived from manufacturing scrap that retain 100% possess the ability to be utilized in new composite components for a variety of applications.

Characterization of Reclaimed Carbon Fibers and their Integration into New Thermoset Polymer Matrices via Existing Composite Fabrication Techniques

by

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DEDICATION

Not to UNC @ Chapel Hill.

BIOGRAPHY

Brian Edward Allen was born to Don and Hilda Allen January 29, 1984 in Atlanta, GA. His older sister, Emily, is nearly two years older than him. The family moved to Switzerland for three years, and then moved to High Point, NC. Brian attended Southwest Guilford High School and then furthered his education at North Carolina State University in 2002. He obtained a B.S. degree in Materials Science and Engineering in 2006. Brian expects to obtain a M.S. under the guidance of Dr. Jerome J. Cuomo in May of 2008.

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1.1 Composite Materials

Composite materials consist of a bulk phase, known as the matrix, and a reinforcement material, typically of fibrous form. The matrix encapsulates the reinforcement material integrally binding the reinforcement together so as to effectively introduce external loads to the reinforcement and protect it from adverse environmental effects.[1] The matrix is bound to the reinforcing fiber to produce a structurally sound composite. In some cases additives or fillers are formulated with the matrix and reinforcing material. These fillers may be cheap mineral powders to extend the resin or have some other function such as fire retardants.[2]

Table 1 shows the common acronyms for composites with respect to their reinforcement material as well as the matrix used in the composite. The abbreviations for the composites are commonly used throughout literature and the industry. Carbon fiber reinforced plastics (CFRP) will be the focus of this work, with an emphasis on recycled carbon fiber reinforced plastics (R-CFRP).

Table 1 – Abbreviations for common composite materials with their respective matrices and reinforcement material

Abbreviation	Composite Name	Matrix	Reinforcement Material
CFRP	Carbon Fiber Reinforced Plastic	Plastic	Carbon Fiber
R-CFRP	Recycled Carbon Fiber Reinforced Plastic	Plastic	Recycled Carbon Fiber
GFRP	Glass Fiber Reinforced Plastic	Plastic	Glass Fiber
CMC	Ceramic Matrix Composites	Ceramic	--
MMC	Metal Matrix Composites	Metal	--

1.1.1 Matrix Materials

A majority of composites fabricated today use polymer matrices. However, other types of matrices utilize metals and ceramics. Metal and ceramic based composites are typically used for structural composite applications. Matrices reinforced with carbon fibers include Al, Mg, Cu, Ni, Ti, Pb, and Sn alloys.[3] Although they are not used as much as polymer matrices, metal and ceramic matrix composites still exhibit similar properties to plastic matrices. However, polymer matrices will be the focus of this research.

Polymer based matrices are used for their excellent structural capabilities including corrosion resistance, electrical insulation, reductions in tooling and assembly costs, and many more.[1] The two main types of polymer matrices are thermoplastics and thermosets. Thermosets are more prevalent in the composites industry and are used mainly for structural applications. However, thermoplastic resins have been used increasingly due to their advantages such as toughness, long shelf life, simplicity of the chemistry, processing time and environment, and recyclability.

Two types of plastics, commodity and engineering, are used depending on the application. Commodity plastics are not used in structural applications and are often used for items such as food packaging. Engineering plastics are used for more structural related applications, possessing properties that enable them to replace traditional construction materials, e.g., metals and woods, in load bearing applications even without reinforcement.[1]

When selecting an engineering plastic for use in a composite application, there are many factors one needs to consider. The engineering plastic must be compatible with the reinforcement material in terms of bonding, thermal properties, mechanical properties, and cost effectiveness. Additionally, the engineering polymer needs to be easy to process with respect to viscosity of the plastic, processing time, and processing temperature.

The most common forms of thermoset polymers are unsaturated polyesters, epoxies, vinyl esters, and phenolic resins. Thermosets are differentiated from thermoplastics because they require curing, causing the polymer chains to crosslink and the plastic to harden. The workhorse of thermoset matrices is unsaturated polyester (UP) which offers an attractive combination of low price, reasonably good properties, and uncomplicated processing.[1] However, epoxies offer better mechanical properties and higher temperature tolerances. Epoxies are found more often in higher performance applications such as aerospace, defense, and sporting goods applications.

Epoxy resins are by far the most widely used polymer matrix for carbon fiber reinforced plastics and currently constitute over 90% of the matrix resin material used in advanced composites.[4] Epoxy resins are heavily utilized in this research. Vinyl ester resins, also used in this research, have properties that are between those of polyesters and epoxies,

with better chemical resistance than polyester resins.[5] Phenolic resins are cured by a condensation reaction using hot press molding and are relatively cheap, having good high temperature performance (230°C), excellent fire and smoke resistance, and good resistance to acids.[5] Phenolic resins will also be used in this research.

Thermoplastics are a type of polymer that has long molecules containing only secondary bonding, allowing them to be melted when heated. Typical thermoplastics include polyethylene (PE), polypropylene (PP), polyamide (PA), polyethylene terephthalate (PET), polyphenylene sulfide (PPS), polyether ether ketone (PEEK), and polyether imide (PEI), to name a few.

The higher end thermoplastics, such as PEEK and PEI, have much higher melting temperatures compared to lower performing thermoplastics such as polyethylene and polypropylene. PEEK has a melting temperature of 345°C, whereas PP has a melting temperature in the range of 165-175°C. The higher temperature resistance of engineering plastics, such as PEEK and PEI, compared to thermoplastics, such as PP, cause it to command a much higher market price.

1.1.2 Carbon Fiber Reinforcement Material

Carbon fibers are produced from one of three main types of precursor materials. These precursors include polyacrylonitrile (PAN), pitch, and rayon. PAN-based carbon fibers are the dominant class of structural carbon fibers and widely used in military and commercial aircraft, missiles, and spacecraft structures. Pitch-based carbon fibers generally have higher stiffness and thermal conductivities, making them useful in satellite structures

and thermal-management applications such as space radiators and electronic enclosures. Rayon-based carbon fibers are not used for structural applications, but their low thermal conductivity makes them useful for insulating and ablative applications such as rocket nozzles, missile reentry vehicle nosecones, and heat shields.[6] Figure 1 reveals the manufacturing processes for PAN and pitch-based carbon fibers.

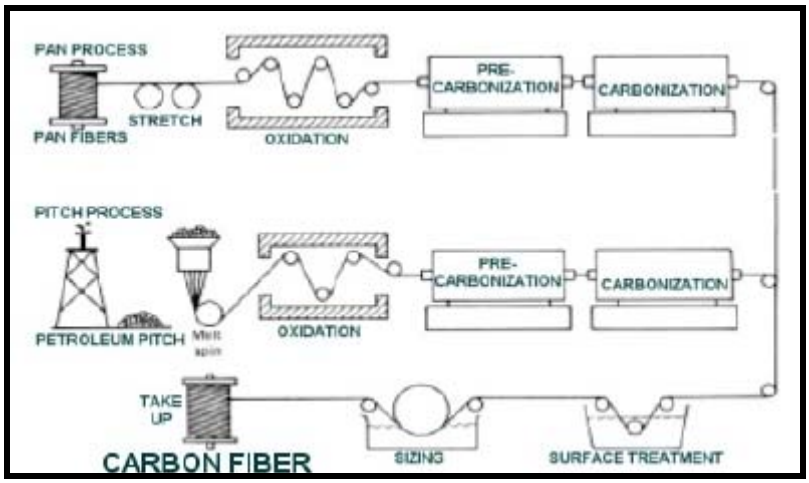

Figure 1 – The PAN and pitch process for manufacturing of carbon fiber[7]

This research focuses on carbon fibers derived from a PAN precursor. To manufacture PAN-based carbon fibers, the polyacrylonitrile is first mixed with water and water-soluble polyethylene glycol (PEG). The mixture is then melt-spun and acrylic PAN precursor fibers are produced. The noncircular/multilobal carbon fiber reinforced composites have better strength and elastic moduli than circular fiber reinforced composites. Additionally, they exhibit a greater surface area which provides better adhesion with a matrix.[8] These multilobal sections appear as striations on the carbon fibers which are revealed in electron micrographs in this research.

Following the melt-spinning of the PAN precursor, the acrylic fibers are then stretched. Stretching of the fibers generally improves the orientations of the molecular chains in the direction of the fiber axis.[8]

The fibers are then oxidized from 205-240°C in an oxidizing environment (air) to crosslink the polymer, ensuring the fibers do not melt during subsequent processing steps. The fibers are held under tension for approximately 24 hours.

The next step in the fabrication of carbon fibers is the carbonization stage to remove the non-carbon atoms. This process occurs at approximately 1500°C. An inert environment is used so only carbon atoms are present in the structure of the fibers.

Graphitization of the fibers forms in an inert environment at approximately 1800-3000°C. The heat treatment of the fibers improves the crystalline structure, thus improving the tensile modulus of the fibers along with the elasticity. The graphitization also eliminates impurities within the fibers.

Following carbonization and graphitization, the fibers are dipped in a surface treatment bath to improve the fiber to resin adhesion in the end composite component. In most cases, the fibers have a sizing applied to them, causing the individual fibers to stick together forming one single filament composed of thousands of individual fibers. This single filament is referred to as tow. Typical tow sizes range from 3K (3,000 fibers in one filament) to 48K. Most production uses tow sizes ranging from 12K to 24K. After the fibers are sized, they are wound on a spool as continuous fibers for use in composite fabrication.

1.1.3 Fillers / Additives

Fillers or additives are commonly combined with the resin and carbon fibers to alter the properties of the composite. For instance, an additive is combined to improve the UV resistance of the composite, protecting it from harmful UV rays which tend to embrittle and discolor most polymeric materials. Among the properties that may be altered with additives or fillers are processibility, mechanical properties, electrical properties, shrinkage, environmental resistance, crystallization, temperature tolerance, fire tolerance, color, cost, and volatile evaporation.[1] Typical fillers include calcium carbonate, kaolin (hydrous aluminum silicate), aluminum trihydrate, and calcium sulfate.

In many aerospace applications, fillers and additives are combined with the composite constituents for fire tolerance. Flame, smoke, and toxicity (F.S.T.) requirements of materials in the aerospace industry are quite stringent. Common fillers used for fire retardance are aluminum trihydrate and calcium sulfate. These additives are used to produce water on the surface of the composite at ignition temperature, produce a surface char that is impenetrable to oxygen, or produce free radicals that react with the surface oxygen, thus starving the fire.[1]

Cost is also a major issue in material selection of a particular component. Composites are typically more expensive compared to alternative materials, such as aluminum, due to the higher costs of the carbon fibers and resin. Therefore, fillers such as calcium carbonate are used in place of some resin to produce a cost effective component.

1.2 Comparable Materials

Material selection is an integral factor in part design to take advantage of specific

material properties. Carbon fiber reinforced plastics are typically used in applications where weight savings are desired. CFRPs have similar mechanical properties to many metals and their alloys, yet are much lighter. Figure 2 reveals that a CFRP, comprised of 60% carbon fibers by weight, has about the same tensile strength (800MPa) as a Titanium alloy, yet is three times lighter. Also the same CFRP, with a specific gravity of 1.53g/cm^3, compared to a GFRP comprised of 55% glass fibers by weight at the same specific gravity, has 2.5 times the tensile strength. This shows the mechanical properties of carbon fiber composites are superior to glass fiber composites.

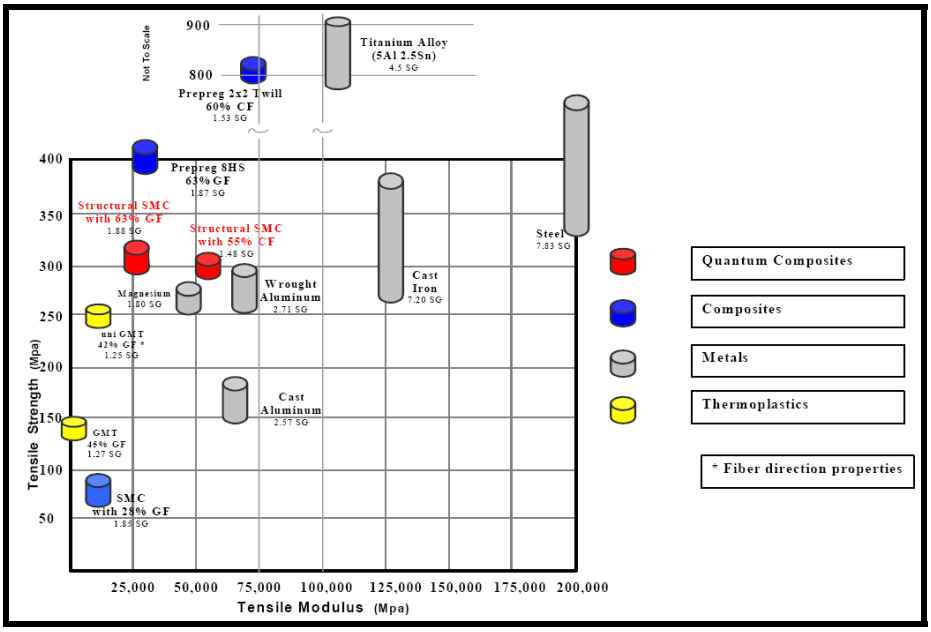

Figure 2 – Chart comparing the tensile strength and modulus of CFRPs to other materials[9]

1.3 Carbon Fiber / CFRP Market Overview

Annual worldwide sales of virgin carbon fiber exceed $1 billion with about $7 to $11 billion in annual sales attributed to CFRP component manufacturing.[10] In 2004 an estimated

22,000 metric tons of CF were consumed worldwide, and about 8,400 tons (about 18.5 million pounds) were consumed in the United States alone.[11] The carbon fiber market has been rapidly growing at a rate of 10% to 14% per year.[12] Figure 3 shows the carbon fiber industry growth projected to 2008. This chart illustrates considerable growth in the carbon fiber industry since the 1970's. Furthermore, the price of carbon fibers has dropped drastically since that time. By 2010 it is estimated that worldwide carbon fiber consumption will be about 40,000 tons.[13] Of this CF consumption, about 40 percent is used in the aviation and aerospace industries.

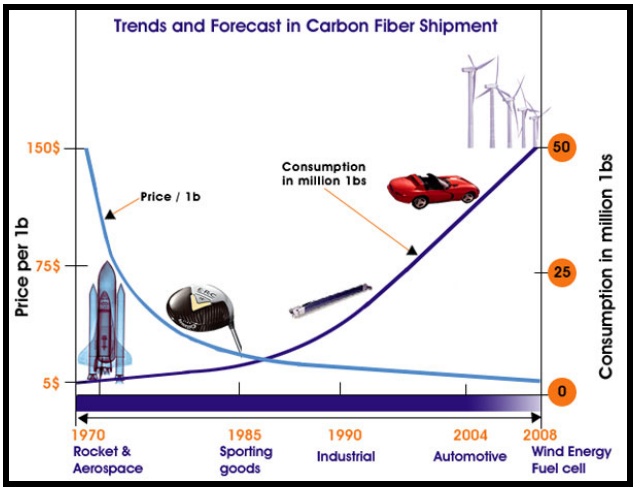

Figure 3 – The long term growth of the worldwide carbon fiber industry[14]

The demand for carbon fiber is certainly increasing, and a market study published in December 2007 projects the total global demand for carbon fibers will more than double from 2006 to 2014. Figure 4 depicts the table excerpted from the market demand study.

	2006	2007	2008	2009	2010	2011	2012	2013	2014
Aerospace	5,210	5,830	7,250	9,120	10,700	11,375	12,230	12,870	13,580
Industrial	15,840	18,285	21,215	24,255	27,270	30,690	34,250	38,405	42,445
Sports	6,500	6,750	7,025	7,485	7,970	8,285	8,680	9,015	9,400
Total	27,550	30,865	35,490	40,860	45,940	50,350	55,160	60,290	65,425

Figure 4 – Projected global carbon fiber demand in metric tons[15]

Although the aerospace industry does not account for the greatest demand for carbon fibers, the industry still uses a considerable amount of CFRP. Total aviation and aerospace carbon fiber demand is projected to increase by 10%-17% annually in the near future with potential demand accelerating in the latter years as new models go into production.[16]

The new Boeing 787 Dreamliner will have greater than 50% carbon fiber reinforced composites, corresponding to about 23 tons of carbon fiber per aircraft. This current demand by the U.S. aviation industry corresponds to about 8 million pounds per year of virgin carbon fiber. Figure 5 shows the material selection of the Boeing 787 Dreamliner's body. The figure also shows that the Boeing 777 used only 12% composite materials. This is a substantial increase in composite use as the major material selection for the aircraft.

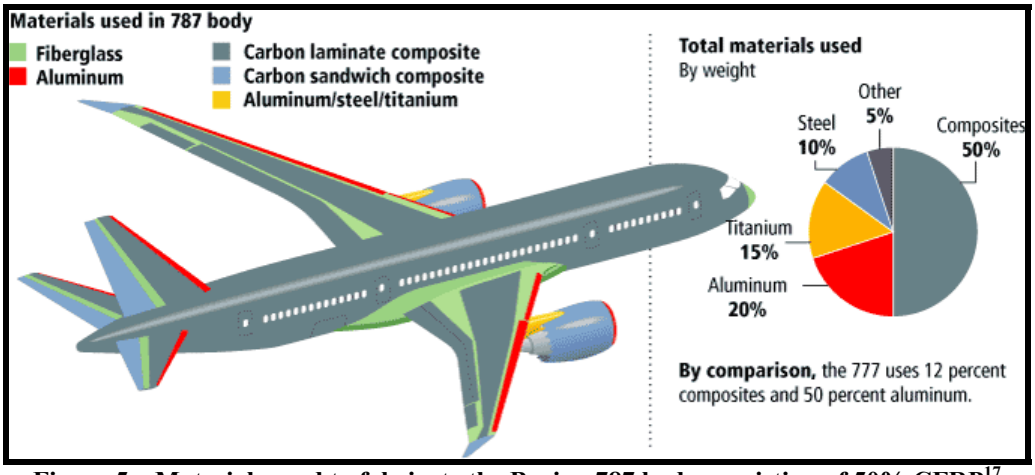

Figure 5 – Materials used to fabricate the Boeing 787 body consisting of 50% CFRP[17]

Boeing is not alone in fabricating its aircraft with composites. European airplane manufacturer Airbus is also incorporating large amounts of composite materials into their A380 aircraft. Glass reinforced aluminum (Glare) is their initial material selection. The A380 also uses conventional composite structures. For instance, use of carbon fiber reinforced plastic for 40% of the wing box saves 1.5 metric tons, cutting the weight of the fully equipped structure to 11.6 metric tons.[18]

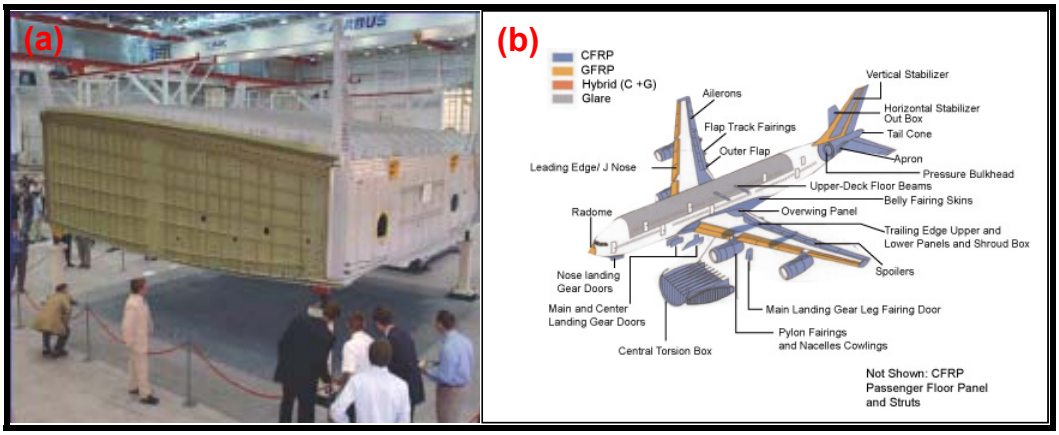

Figure 6 – (a) Airbus A380 central wing box consisting of CFRP material, (b) Airbus A380 body utilization of composite materials[18]

As the demand is projected to continually rise, carbon fiber and CFRP will no longer be considered an exception or exotic material but rather a commodity engineering material. Currently CFRP waste is being landfilled. Therefore, as the material supply grows, recycling of composites becomes a necessity.

A model suggests that as the composite material is utilized in increased quantities, there will be manufacturing wastes generated as well. Depending on part design, process, and learning curve, manufacturing excess as a percentage of purchased weight can vary. For

discussion's sake a manufacturing excess of 10% has been used in the model to generate a conservative estimate of the near term potential available carbon fiber from aviation and aerospace applications.[19] Figure 6 shows the possible material supply of recycled carbon fibers (pink line). Assuming a conservative 10% demand, there is still a considerable waste stream stemming from manufacturing scrap.

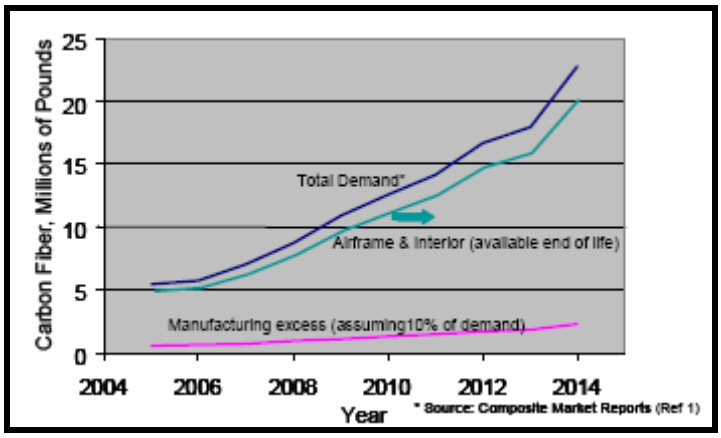

Figure 7 – Commercial transport carbon fiber demand and potential recycling availability[19]

2. Composite Recycling

2.1 Motivation for Recycling Composite Material

As the CFRP market continues to grow, so does the composite waste accumulated. Reclamation techniques and infrastructure need to be commercialized in order to re-use the material rather than putting it into landfills. Research has proven the constituents of composite materials still retain some value and can be recycled. Instead of discarding this valuable material, in this case carbon fibers, the carbon fibers can be recycled and reintroduced into new composite components.

2.2 Legislation for Recycling Composite Material

The European Union is very strict about reclamation of composites, specifically in the automotive sector. Recently established EU Directive 1999/31/EC EU, Directive on Landfill of Waste, claims a considerable reduction of waste comprised of organic material will be realized.[20] Furthermore, another directive deals with vehicles that have reached their end-of-life (EOL). The End-of-Life Vehicles Directive, EU Directive 2000/53/EC, places stringent demands on automobile manufacturers requiring the following:

- After 2006, 85% of the weight of all end-of-life vehicles must be re-used, recycled, or subject to energy recovery and only 15% may be disposed in a landfill
- After 2015, 85% of the weight of all end-of-life vehicles must be re-used or recycled, a further 10% may be subject to energy recovery, and a maximum of 5% of the vehicle may be disposed of in a landfill
- After 2007, it is the responsibility of the vehicle manufacturer to dispose of a vehicle[21]

Here, the EU is enacting the "cradle-to-grave" policy, forcing the fabricator of an automobile to be responsible for the vehicle from its creation all the way to its end of service. As automobile manufacturers are increasingly using composites to fabricate parts a commercialized technology for reclamation of composite parts is necessary. Industries are continuing to become more environmentally friendly, and the technology needed to recycle an increasing material supply has to progress as well.

2.3 End-Of-Life Aircraft Recycling Organizations

As countries have stiffened their stance on landfilling of organic materials, the two largest airplane manufacturers in the world, The Boeing Company and Airbus, have generated organizations to address this issue.

2.3.1 Aircraft Fleet Recycling Association (AFRA)

The Aircraft Fleet Recycling Association (AFRA), led by Boeing, is an international association aimed to improve aircraft industry sustainability by promoting safe and environmentally proactive management of the world's aging aircraft fleet. AFRA's main goals are to

- Safely and economically return aircraft to revenue service
- Safely return engines and parts to the world fleet
- Safely return reclaimed materials back into commercial manufacturing.[22]

The third point emphasizes reclamation of aviation and aerospace materials and reintegrating them back into the commercial sector. AFRA represents a wide range of the aviation spectrum including composite recyclers, scrap consolidators, and engine manufacturers. All the members have the same goal of reintroducing EOL material back into commercial manufacturing with an organized and efficient effort.

2.3.2 Process for Advanced Management of End-of-life Aircraft (PAMELA)

The Process for Advanced Management of End-of-life Aircraft (PAMELA) is headed by Airbus and supported by the European Commission. The European Commission selected

the PAMELA project for its LIFE (l'Instrument Financier pour l'Environnement) program, created to assist the development of solutions to environmental problems facing the EU. PAMELA's main objective is to set a benchmark for the safe and environmentally friendly management of EOL aircraft, covering the whole process from storage at decommissioning, disassembling, and dismantling to the recycling or elimination of constituent materials.[23]

Airbus, like Boeing, has recognized the increase in composite material being generated by their production facilities and the environmental implications of landfilling these materials. Today, EOL aircraft are scrapped for parts, used for training, or placed in aircraft salvage yards. By assembling the right companies and organizations, the two competing aircraft manufacturers are becoming more progressive in the recycling realm.

2.4 Infrastructure/Economics of Recycling Composites

Composite recyclers have recognized the abundance of composite scrap material and developed numerous technologies for recycling composites and reclaiming the carbon fibers. It is pertinent that recovering carbon fibers is economically feasible and the RCFs have a desirable next use. The costs of recycling principally arise from collection, transportation, and processing.[24]

2.4.1 Composite Waste Stream Forms

Composite scrap exists in the form of part trimmings, off-cuts, expired prepreg, cured out of spec. parts, or EOL material. Prepreg is material containing both carbon fiber and partially cured resin, typically epoxy, which has been pre-impregnated into a carbon fiber

preform. Such composites are fabricated by laying the fibers parallel and saturating them with resinous material that holds the fibers together.[6] This material form is used to lay up on a mold or tooling board and then cured under heat and pressure in an autoclave, forming a composite part. When the patterns are cut out for lay-up, the rest of the material is denoted as part trimmings scrap and discarded. Prepreg cutting waste typically amounts to 25-50% of the material.[24]

Figure 8 shows skid boxes full of composite manufacturing scrap. This prepreg material has different colored release paper to identify the type of resin and carbon fibers.

Figure 8 – Skid boxes containing prepreg manufacturing composite scrap material

Prepreg is initially malleable and can easily take the shape of the mold. Prepreg also needs to be kept at a particular temperature, typically 0°F, so it does not cure and harden. If prepreg is not stored properly it expires and is designated as scrap material. Figure 9a shows a roll of expired scrap prepreg.

Other types of manufacturing scrap exist in the form of cured parts generally derived from composite components which are not within the tolerances of the desired specifications. An example of a composite panel which is out of spec. is shown in Figure 9b.

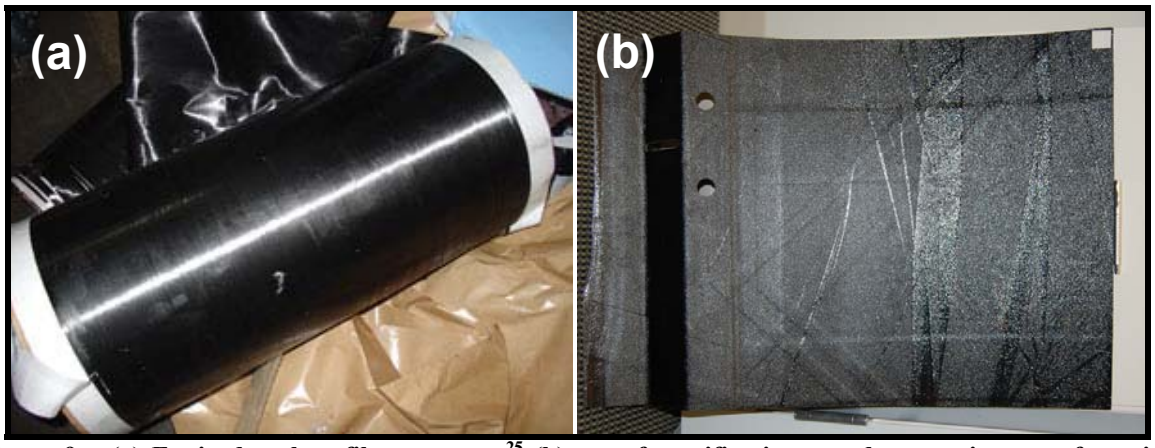

Figure 9 – (a) Expired carbon fiber prepreg,[25] (b) out of specification cured composite manufacturing scrap panel for military use

Figure 10 shows the distribution of advanced composite manufacturing waste by type of material. It should be noted that end-of-life scrap is not listed in this distribution because it is not derived from manufacturing scrap. Prepreg material completely dominates the percentage of manufacturing waste at 66%.

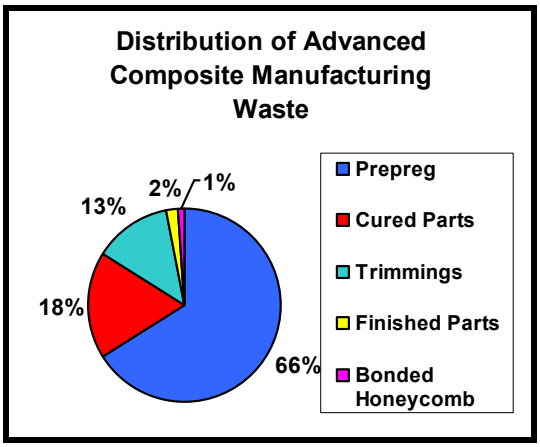

Figure 10 – Distribution of advanced composite manufacturing waste stream [24]

End-of-life composite materials are parts that have been used until failure or are obsolete in their respective industry. This composite scrap is no longer used or needed. Although there are multiple industries in which the composite EOL waste exists, the aerospace industry is normally thought of when dealing with EOL scrap material. Figure 11a shows an EOL stabilizer for an F-18 fighter jet in a scrap yard.

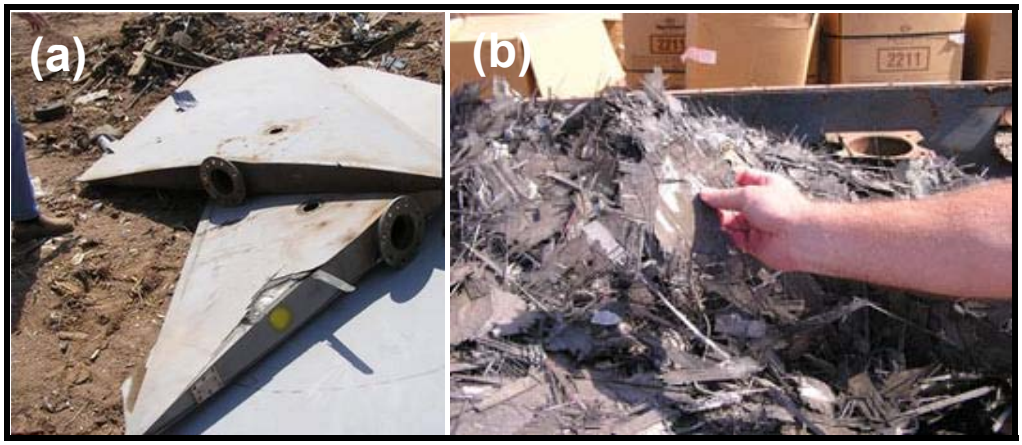

Figure 11 – EOL composite scrap which is in a scrap yard, (a) F-18 stabilizer, (b) hammermilled composite scrap ready to be recycled[25]

2.4.2 Composite Scrap Collection / Sorting

To produce an efficient system of recycling composite scrap, recyclers and scrap producers need to collaborate. This starts at the collection and sorting stage. As the composite scrap is segregated from the other waste streams, it is important that the manufacturer sort the material and inform the recycler of the resin type used in the composite scrap. This is necessary because some types of resin are more difficult to recycle due to their higher melting temperatures (e.g., bismaleimide resins). Companies that recycle can receive public relations benefits and "green points" for recycling their composite material rather than landfilling it.

2.4.3 Transporting Composite Scrap

Recyclers can purchase scrap material from the manufacturers for a small fee, or even free of charge, eliminating the cost to discard the material. The recycling effort should be located in an area generating large quantities of composite scrap to reduce transportation costs. For instance, it would be highly inefficient for a composite recycler to be located in Maine, where little carbon fiber scrap is produced, while its main source of composite scrap exists in Washington. Figure 12 reveals major carbon fiber and CFRP producers, recyclers, and scrap consolidators in the U.S.

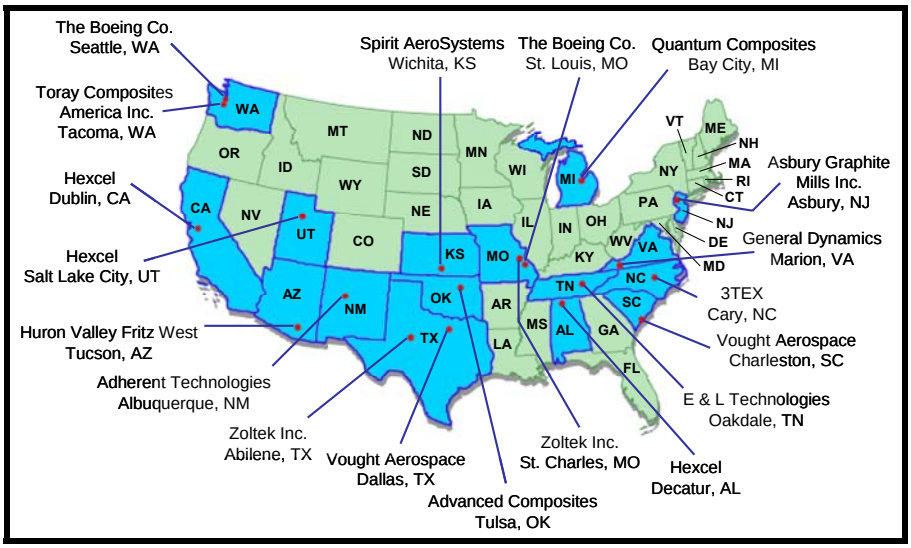

Figure 12 – Composite networking throughout the United States including carbon fiber manufacturers, composite manufacturers, recyclers, and scrap consolidators

2.4.4 Processing Composite Scrap

The collection, sorting, and transporting sectors are all important steps in developing a material supply to recycle. However, the processing costs of reclaiming the carbon fiber are of the utmost importance. The economics of producing RCFs need to be feasible for reclaimed carbon fibers to compete with alternative materials in the marketplace.

A reclamation process needs to be energy efficient to reduce costs. It also needs to be versatile, supporting various types of waste streams (manufacturing and EOL scrap). Most importantly, the process must produce undamaged RCFs which are quite comparable to virgin carbon fibers with respect to surface and mechanical properties.

2.5 CFRP Recycling Techniques

Multiple composite reclamation techniques exist to recover carbon fibers from composite scrap material. These techniques include, but are not limited to, pyrolysis

processing, catalytic conversion processing, vacuum pyrolysis, fluidized bed treatments, microwave treatments, supercritical fluid treatments, chemical treatments, thermal shock, and grinding the CFRP material. Pyrolysis, catalytic conversion, fluidized bed processing, and microwave treatments are processes that are currently being investigated thoroughly for commercialization, especially by the aerospace industry.

2.5.1 Pyrolysis Processing

Milled Carbon Ltd. (Birmingham, UK), a current member of AFRA in collaboration with Boeing, uses a continuous pyrolysis process to reclaim carbon fiber. Milled Carbon Ltd. has developed a continuous pyrolysis process that removes all resins and binders resulting in an unsized recyclate that can be milled or chopped.[26] This technique essentially burns off the polymer matrix and frees the carbon fibers using elevated temperatures. Figure 13b shows carbon fiber material that is extracted from their proprietary process. The original composite component was a Rolls-Royce Trent engine (Figure 13a).

Figure 13 – (a) Rolls-Royce Trent engine bypass, (b) recovered carbon fiber[26]

Reclaimed carbon fiber derived from Milled Carbon Ltd.'s continuous pyrolysis process was previously examined by North Carolina State University. The RCFs were recovered from a F-18 stabilizer shown in Figure 14a. The stabilizer was fabricated using Hexcel 3501-6 epoxy resin and Hexcel AS4 grade carbon fiber. The stabilizer was then exposed to a hammermilling process by Huron Valley Fritz West (Tucson, AZ), shown in Figure 14b. The composite was then sorted, separated, and processed using Milled Carbon Ltd.'s reclamation technique producing RCF shown in Figure 14d. This fiber's surface and mechanical properties were characterized and compared to an AS4 virgin control fiber.

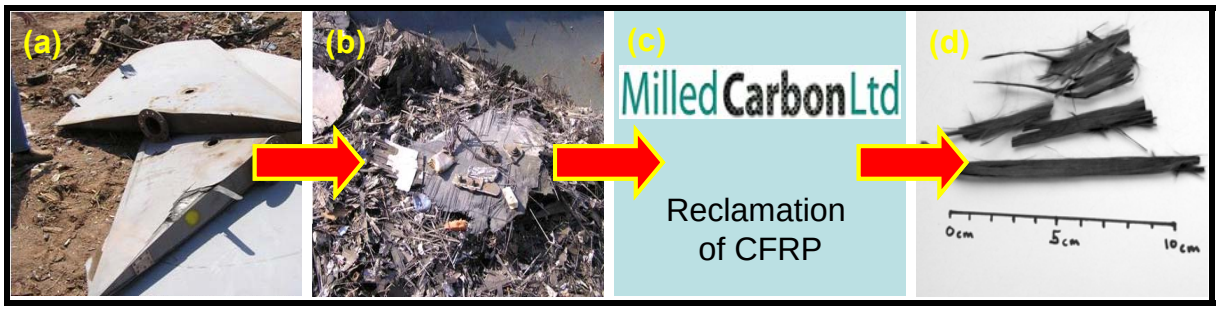

Figure 14 – Milled Carbon Ltd.'s RCF derived from the continuous pyrolysis process

Extensive characterization, including optical and electron microscopy, XPS, and energy dispersive spectroscopy (EDS), was performed by NC State. The recycled fibers examined showed evidence of particulates, trace metals, and differing surface chemistries. Some recycled carbon fiber properties are comparable to those of the virgin fibers.[27] Figure 15a shows that all the resin was not removed from the fiber by the pyrolysis process. The EDS spectra of particulates on the fiber surfaces reveal strong iron and aluminum peaks (Figure 15b). Also, the C 1s peak derived from the XPS data was deconvoluted to determine

the percent functionality on the surface of the fibers (Figure 15c). This showed the carbon fiber reclaimed by Milled Carbon Ltd. had similar functionality on the surface when compared to a virgin AS4 fiber. The work performed by NC State revealed promising surface properties for RCFs compared to virgin carbon fiber.

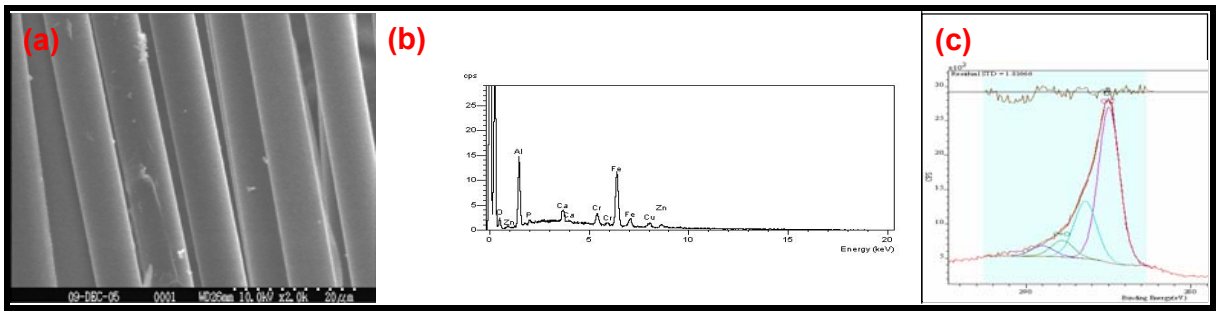

Figure 15 – (a) SEM of CF reclaimed from Milled Carbon Ltd.'s continuous pyrolysis process, (b) EDS spectra of CF surface[27], (c) deconvolution of C 1s peak determining percent functionality on surface of CF

Single fiber tensile testing (SFTT) was also performed by NC State to determine the mechanical properties of single filaments. The RCF derived from the continuous pyrolysis process retained 88% of the ultimate tensile strength compared to virgin AS4 fiber, revealing the process did not significantly reduce the fiber's strength.[28] This mechanical behavior shows potential for RCFs to be used as reinforcement material in composite applications.

2.5.2 Catalytic Conversion Process

Adherent Technologies Inc. (Albuquerque, NM), also a member of AFRA, uses a tertiary catalytic conversion process to reclaim carbon fibers. This process uses a depolymerizing catalyst to extract the carbon fibers from the CFRP. The uniqueness of this process lies in capturing the polymeric material and converting it into low molecular weight

hydrocarbons. The researchers suggest the hydrocarbons can be reused as fuels, monomers, or chemicals.[29] Figure 16 shows the catalytic conversion reactor used to recover carbon fibers from CFRP material. This reactor operates at low temperatures and pressures, typically 150°C and 150 psi.[30]

Figure 16 – Adherent Technologies Inc.'s low temperature, low pressure catalytic conversion reactor[30]

NC State also characterized the fiber derived from Adherent Technologies Inc.'s catalytic conversion process. Figure 17d shows the fiber derived from their proprietary process. The CFRP scrap reclaimed by Adherent was from the same F-18 stabilizer. The fiber morphology derived from the catalytic conversion process is quite different from the continuous pyrolysis process.

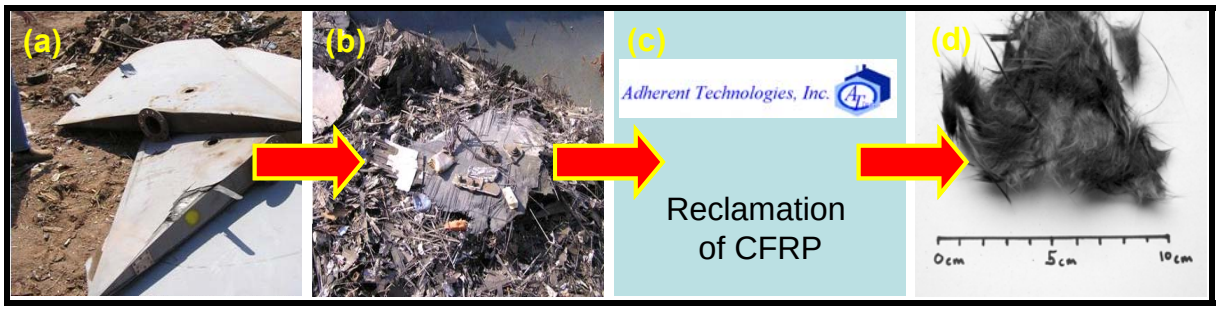

Figure 17 – Adherent Technologies Inc.'s recycled CF derived from the catalytic conversion process

Figure 18 shows characterization performed by NC State on Adherent's reclaimed carbon fiber. The first micrograph (Figure 18a) depicts the random orientation of the fibers when gathered from the reactor. Furthermore, Figure 18b shows there was slight trace metal contamination present. This trace metal contamination is most likely due to the carbon fiber being in the presence of other contaminants when inside the F-18 stabilizer, such as honeycomb core and copper wiring. There was by far less contamination visible in the fibers compared to the CFs delivered from Milled Carbon Ltd. Finally, the carbon peak was deconvoluted to determine the functionality on the surface of the carbon fibers, as shown in Figure 18c. The oxygen containing functional groups of the RCF were similar to a virgin AS4 fiber.

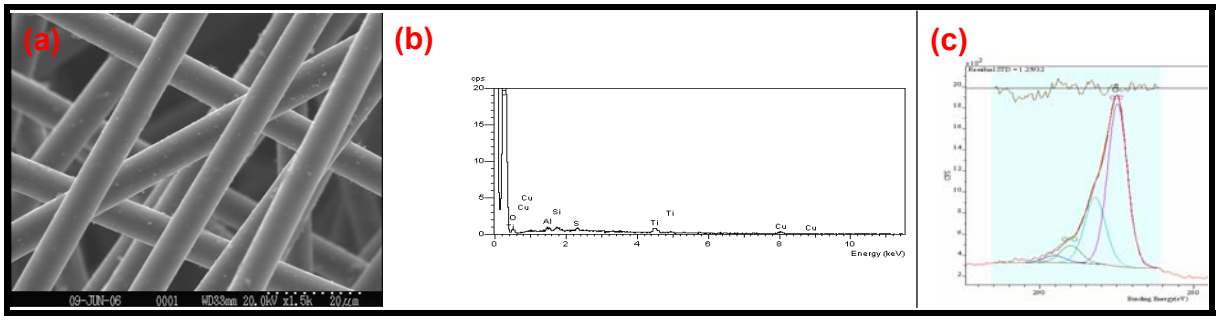

Figure 18 – (a) SEM of CF reclaimed from Adherent's catalytic conversion process, (b) EDS spectra of CF surface[27], (c) deconvolution of C 1s peak determining percent functionality on surface of CF

NC State also characterized the tensile strength of the RCF derived from the catalytic conversion process. The RCF retained 61% of its ultimate tensile strength when compared to a virgin AS4 carbon fiber.[28] This strength decrease can be related to the process conditions the fiber sees when recycling. On the contrary, Adherent Technologies Inc. reports much higher strength retention of their reclaimed carbon fibers when using similar processing conditions.

2.5.3 Vacuum Pyrolysis Processing

Adherent Technologies Inc. also uses a vacuum pyrolysis chamber to reclaim carbon fibers from CFRP scrap. This reactor can handle multiple waste streams, depending on the matrix material, easier than the catalytic conversion reactor. However, the process does not produce 99.5% pure carbon fibers, as there is a slight char on the surface of the fibers. The temperature in the reactor can be adjusted via four gas-fired burners. The scrap is fed into the reactor via an automated conveyor. Extensive measuring equipment for temperature and vacuum complements this pilot scale unit.[30] Figure 19 shows the pilot scale vacuum pyrolysis "Phoenix reactor."

Figure 19 – Adherent Technologies Inc.'s Phoenix reactor, a pilot scale vacuum pyrolysis unit[30]

2.5.4 Fluidized Bed Treatment

The University of Nottingham (Nottingham, UK) uses a fluidized bed process to recover carbon fibers. This group also works in collaboration with Milled Carbon Ltd. analyzing recycled carbon fibers. The objective of the process is to reclaim clean fibers and fillers from a variety of contaminated composite scrap and harness the polymer energy recovery. The fibers, which are reclaimed from the fluidized bed process, are short in length and also random in orientation. The scrap composite is placed in a bed of silica sand fluidized with heated air. During the process the polymer matrix material volatizes leaving recovered carbon fibers. The fibers are separated from the gas stream by a cyclone process. The temperature of the fluidized bed reaches 450-500°C, causing the polymer to not fully oxidize.[31] Figure 20a shows a schematic of the process and Figure 20b shows the actual apparatus used to reclaim carbon fiber.

Figure 20c is an electron micrograph of carbon fibers which are reclaimed from the fluidized bed process. The University of Nottingham also performs extensive work using XPS and interfacial shear strength (IFSS) testing using a procedure called the micro-droplet

test. This micro-droplet test helps determine how the recycled carbon fiber adheres to a droplet of resin.

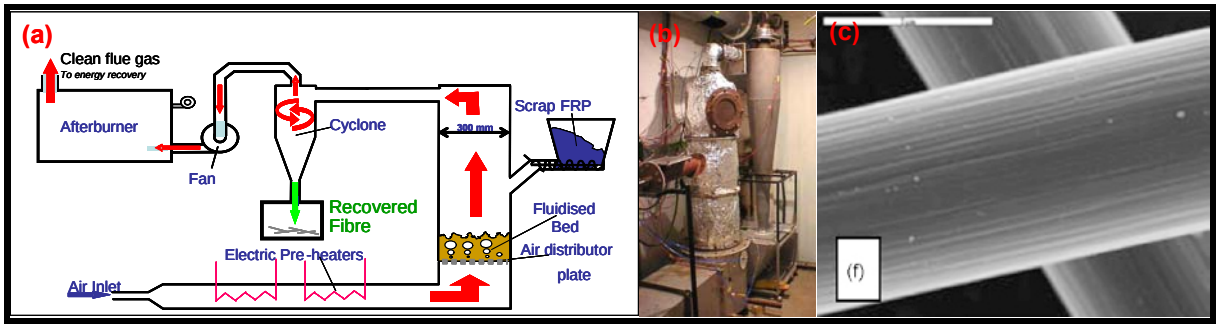

Figure 20 – (a) Fluidized bed process schematic, (b) actual fluidized bed reactor, (c) SEM of MR60H reclaimed carbon fiber from fluidized bed process[32]

2.5.5 Microwave Treatment

A microwave treatment process also exists for recovering carbon fibers from polymer matrix composites. The composites are typically exposed to 3kW for 8 seconds in order to recover the carbon fibers.[33] This process essentially heats the composite from the inside out. Figure 21a shows a generic schematic for reclaiming carbon fibers. An electron micrograph is shown in Figure 21b. Thermogravimetric analysis (TGA) and atomic force microscopy (AFM) were also performed on the fibers for characterization.

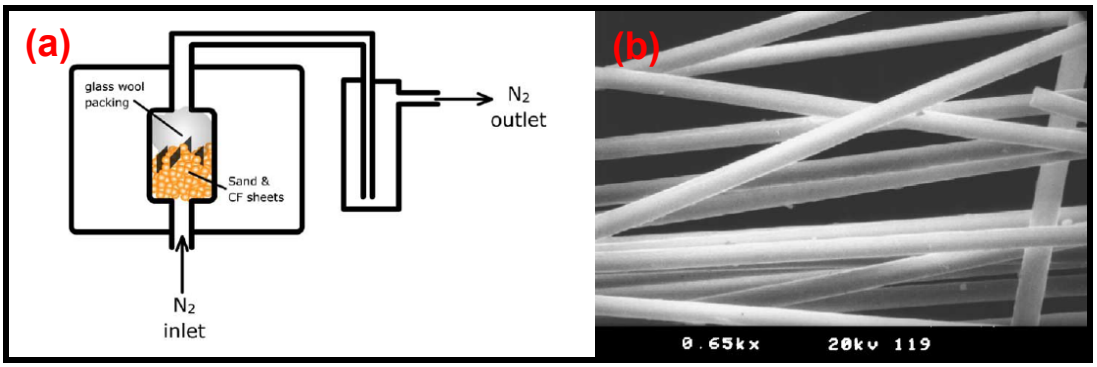

Figure 21 – (a) Schematic of a microwave process for recovery of carbon fibers, (b) SEM of fiber recovered from microwave treatment[33]

2.5.6 Supercritical Fluids

Another technique for recovering carbon fibers from CFRP is through the use of supercritical fluids. The laboratory group at the University of Nottingham, also researching the fluidized bed process, investigated the use of supercritical propanol to remove epoxy resin from the surface of CFRPs. This technique was carried out effectively above 450°C and above 50 bar.[34] The schematic for the supercritical propanol system is shown in Figure 22. Also, electron micrographs shown in Figure 22 reveal very clean fibers with essentially no resin remaining on the surface of the fibers.

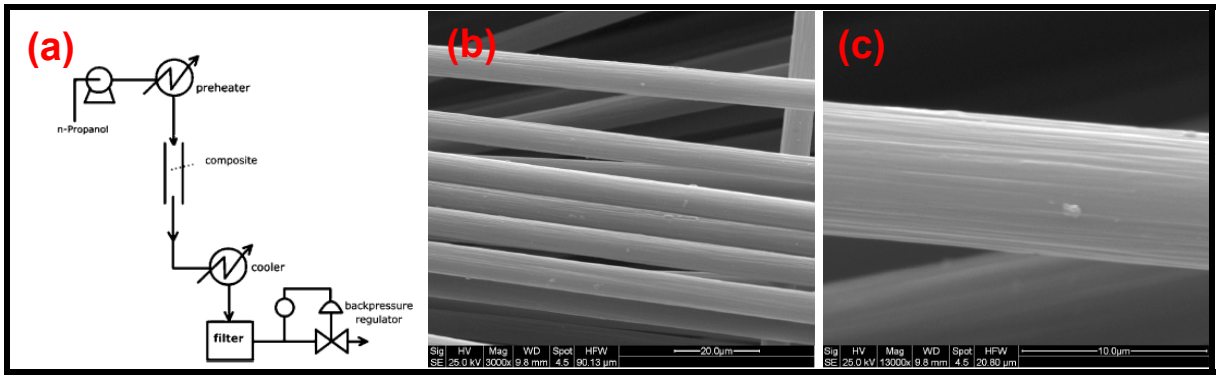

Figure 22 – (a) Schematic for the recovery of CFs using supercritical propanol, (b) electron micrograph of CF reclaimed using supercritical water with alkali catalyst at 3,000X, (c) at 13,000X[35]

2.5.7 Chemical Treatment

The chemical degradation treatment exposes CFRP to solvents, acids, and bases at various temperatures to degrade and break down the polymeric substrate in order to liberate the fibers.[36] The chemical treatment schematic is shown in Figure 23.

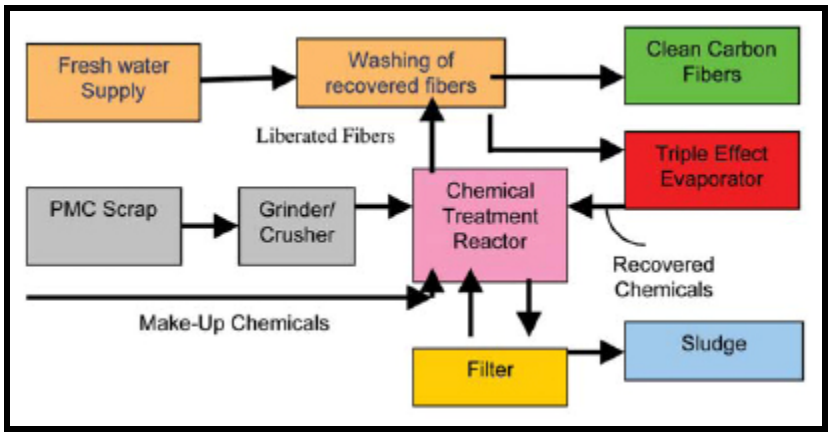

Figure 23 – Chemical treatment method of recovering carbon fibers and then rinsing with water[36]

Study of this process revealed that different chemicals were required to break down the different polymers, rendering the process economically infeasible. The fibers are rinsed with water after the process is completed, and chemical waste is also a problem.

Another technical paper investigated the use of reclaiming carbon fibers using a solvent method in nitric acid solutions. The study optimized the temperature of the solution, (90°C) with a nitric acid concentration of 8M, and a ratio of the sample weight to the nitric acid solution volume 4g:100mL.[37] Electron probe microscopy found the recycled carbon fibers to be clean and undamaged.

2.5.8 Molten Salt Treatment

Reclaiming carbon fibers by molten salt processing, at temperatures anywhere from 400°C to 600°C, uses molten or dissolved salt baths to separate carbon fibers from the polymer matrix.[38] This research is part of the Recycomp project evaluating composite waste of thermoset matrices. Figure 24 shows scanning electron micrographs of carbon fibers recovered from thermoset matrices using the molten salt treatment. It is obvious in the micrographs, particularly Figure 24b, that a large amount of resin/residue and particulates still exist on the surface of the fibers.

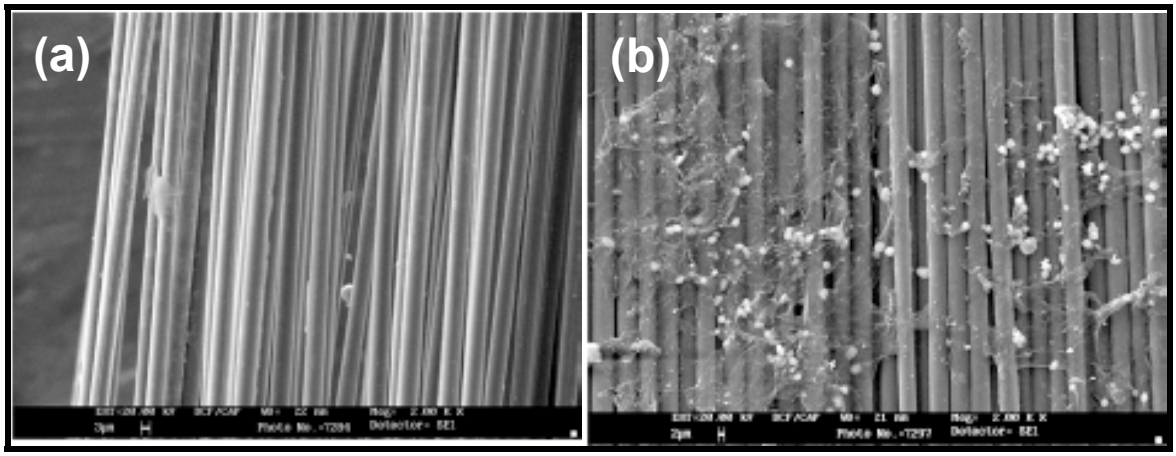

Figure 24 – SEM micrographs of carbon fibers reclaimed from thermoset matrices using molten salt processing[39]

2.5.9 Thermal Shock Treatment

Thermal shock is another treatment which attempted to recover carbon fibers from polymer matrices.[36] The composite panels are dipped into liquid nitrogen and then immediately placed into boiling water. The process, in theory, attempts to leverage the differences in the coefficients of thermal expansion between the polymer and carbon fibers.

However, this technique is normally unsuccessful and fails to produce clean fibers as no real visible separation between the two constituent materials is found.

2.5.10 Grinding of CFRP Material

Grinding CFRP material into a powder-like substance is also used as a recycling technique. This technique uses the ground powder as filler material for processes such as bulk molding compounds (BMC) and sheet molding compounds (SMC).[40,41] To date, this is the easiest way to re-use scrap CFRP material. However, research has shown RCFs retain their mechanical and surface properties compared to virgin fiber. Here, the value of the CFs is eliminated once the CFRP is ground into a powder.

2.6 Recycled CFRP Markets

Recycled carbon fibers are usually milled or chopped. The milled fiber typically has average lengths of 100 - 150μm. Chopped fiber can be anywhere from 1/8" to 1" in average length. Depending on the grade, chopped fiber is normally more valuable than milled fiber due to the length. There are various markets for each of these types of fiber. Although research has shown that recycled carbon fibers retain much of their mechanical properties when compared to virgin fibers, the CFs would not be reused in load bearing structural applications such as a wing on a Boeing 787 Dreamliner.

Milled fiber is used as composite reinforcement for shielding, dissipative, and conductive compounds. The material property of interest is the electrical conductivity of the carbon fiber. If the recycled carbon fiber contains similar conductivity to the virgin carbon

fiber, then it has the potential to replace the virgin material at a reduced cost. Conductive paper applications are also evaluating the use of recycled carbon fibers as well as the fuel cell industry for conductive plating due to carbon fibers' electrical conductivity. This type of material would be reintroduced into polymers using an extrusion line, forming pelletized material and subsequently injection molded into various parts.

Chopped carbon fiber can also be used in electromagnetic interference shielding applications as well as in more conventional components requiring more load bearing. One particular application, which is growing at approximately 50% per year, is the buoyant housing material used for oil drilling. The part manufacturers are in need of a carbon fiber source for the housing due to the difficulty of obtaining virgin carbon fiber. The main material property of interest here is the mechanical strength of carbon fibers used as reinforcement material.

RCFs have the versatility to penetrate different market sectors. Depending on the material property of interest, recycled carbon fibers have the ability to replace virgin carbon fibers, creating a cost effective product. Recycled carbon fibers can also be used as reinforcement material in applications where glass fibers are typically used. However, this is dependent on the price per pound of RCFs compared to glass fibers and also the mechanical enhancement needed. If part manufactures want to replace metals with CFRPs, but the price of virgin carbon fiber is too high, they have the ability to use recycled carbon fibers at a much lower price, therefore benefiting from the properties of the RCFs.

3. Composite Fabrication Techniques

To construct a composite part, multiple techniques are used in industry. Of course, part variability dictates which process to use. Time, cost, intricacy of the part, material selection, and other variables are considered when fabricating a CFRP component. The fabrication techniques used in this research were vacuum assisted resin transfer molding (VARTM), bulk molding compounds, simulated sheet molding compounds, and compression molding. SMC and BMC formulations are used in conjunction with compression molding and have the ability to produce large quantities of composite parts quickly. Heating and pressurizing composite material using an autoclave is prevalent in industry as well. Also, composite pellets can be formed by extruding plastics and carbon fiber together at elevated temperatures. The pellets in turn can be injection molded into the desired mold, thus forming the specific component.

3.1 Vacuum Assisted Resin Transfer Molding

Vacuum assisted resin transfer molding is used to produce composite parts by drawing a vacuum on the reinforcement material and subsequently infusing resin through the material using a bagging film which is vacuum sealed. A process which is virtually identical is known as Seeman Composite Resin Infusion Molding Process (SCRIMP). The SCRIMP process is prevalent in the marine industry where masts of over 75ft have been fabricated. The VARTM process was scaled down considerably in this research, fabricating composite panels of $1ft^2$ in area. Figure 25 reveals the schematic of the VARTM setup used to fabricate CFRP panels in this research.

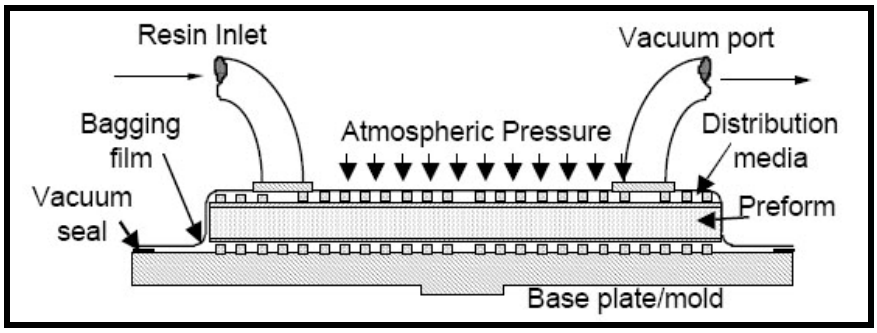

Figure 25 – VARTM schematic used for fabrication of composite panels infusing resin between the carbon fiber reinforcement with the assistance of a vacuum

3.2 Bulk Molding Compounds

Bulk molding compounds consist of a mixture of reinforcement material, usually fiberglass or carbon fibers, a resin, filler, mold release, and a catalyst. These ingredients are added to a high shear batch-type mixer, typically a Sigma blade mixer (Figure 26a) and mixed together until forming a dough-like compound (Figure 26b) called logs or charges. The charge is then weighed and placed into a mold for compression molding (Figure 26c). Here, the BMC is heated and pressurized at a part specific curing time, causing the composite to harden. The advantage of using a BMC to formulate parts is the ability to fabricate highly detailed parts consisting of thick and thin sections. Traditional markets served with bulk molding compounds include satellite, aerospace and defense, commercial aircraft, industrial, consumer, and sporting good applications.

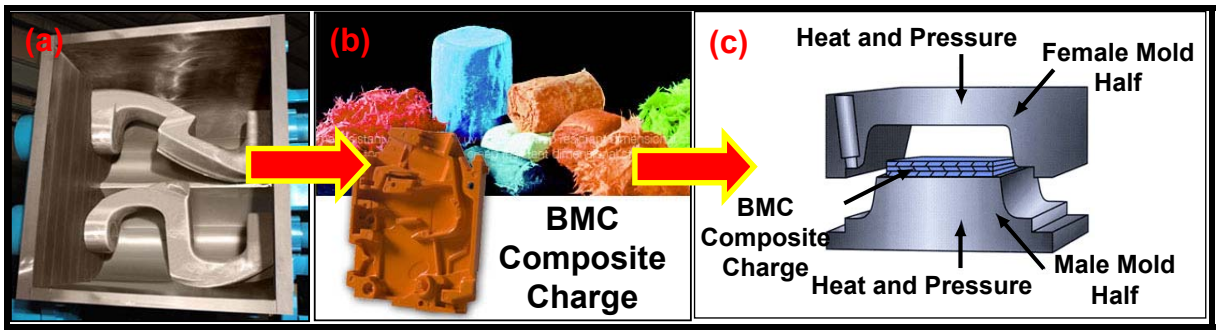

Figure 26 – A BMC sequence, (a) sigma blade mixer, (b) the BMC composite charge, (c) compression molding the BMC charge into the desired component

3.3 Sheet Molding Compounds

Sheet molding compounds can be used to fabricate composites using either carbon fiber or fiberglass as the reinforcing material. This process is used for thermoset resins. Multiple spools of fiber are fed into rotating chopping blades. The fibers are fed at a constant speed producing fibers of a desired length. A doctor box is filled with the resin and a thin layer is applied to a carrier or release film. The fibers fall onto the lower layer of resin in a random orientation as shown in Figure 27.

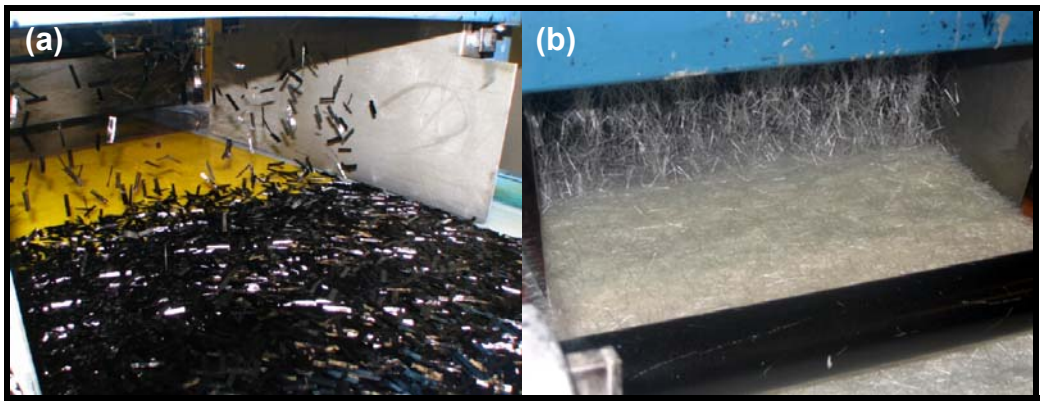

Figure 27 – (a) Carbon fiber reinforcement material and (b) fiberglass reinforcement material for a sheet molding compound[9]

Another doctor box located atop the fibers applies another thin layer of resin on a carrier film

atop the fibers, essentially creating a sandwich structure. The layers are then passed through compaction rollers infusing the fibers with the resin. This process thus creates a sheet molding compound. The SMC is then moved down the line to heat, cool, and then package. A schematic of a sheet molding compounder is seen in Figure 28.

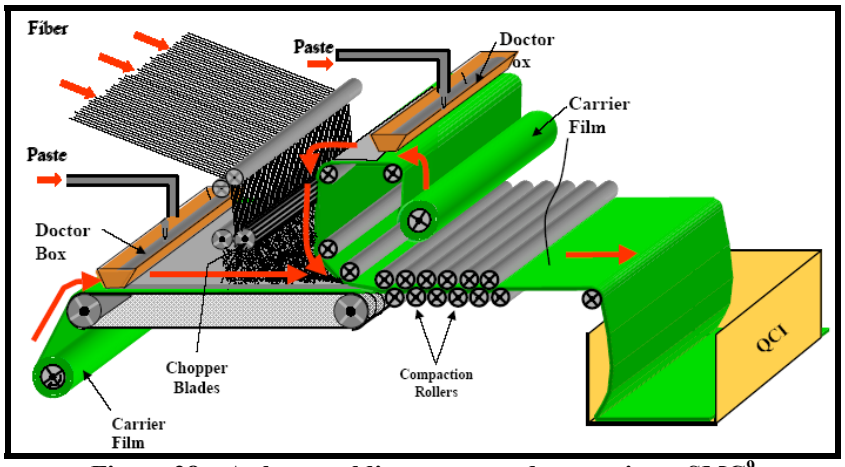

Figure 28 – A sheet molding compounder creating a SMC[9]

After the sheet molding compound has been formed, it is used in the same manner as a BMC charge. The SMC is placed in a compression molding apparatus, heated, and pressurized, producing a cured composite component.

3.4 Compression Molding

Compression molding is a technique used to fabricate composites utilizing heat and pressure. A SMC or BMC charge is placed in the bottom part of a mold and then the mold is closed. The part is cured for the desired time, depending on the size, using heat and pressure. Figure 29 shows a schematic for compression molding.

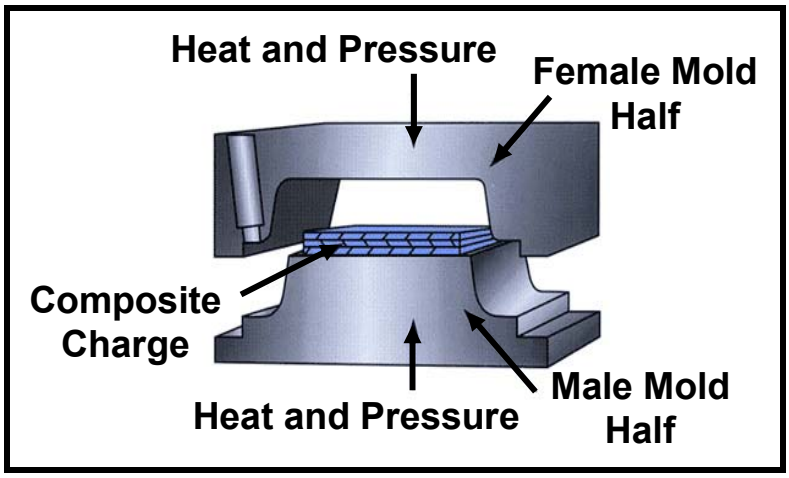

Figure 29 – Compression molding schematic heating and pressurizing a composite charge to fabricate a cured composite part

Obviously the temperature, pressure, curing time, and weight of the charge differ depending on the composite part constructed. In this research a 30g charge was used and heated to approximately 160°C at 2200psi for no longer than 5 minutes, utilizing carbon fibers and a phenolic resin. The curing cycles are specific for different resin systems as well.

3.5 Extrusion / Injection Molding

Extrusion of composite material is subsequently followed by injection molding. First the composite must be extruded by mixing the fiber and plastic. Figure 30 shows a typical extruder used for CFRPs.

Figure 30 – An extruder where polymer pellets and reinforcing fibers are inserted and then mixed together within the apparatus and forced through a die to be pelletized for injection molding

In this figure, the polymer pellets would be inserted along with the reinforcement material, then mixed and sheared within the apparatus at elevated temperatures. Typically twin screws are used to mix the material within the apparatus. The material is then forced through a die and the molten CFRP strand is pulled through a water bath. The material is then drawn into a pelletizer (Figure 31a) and CFRP pellets are formed (Figure 31b).

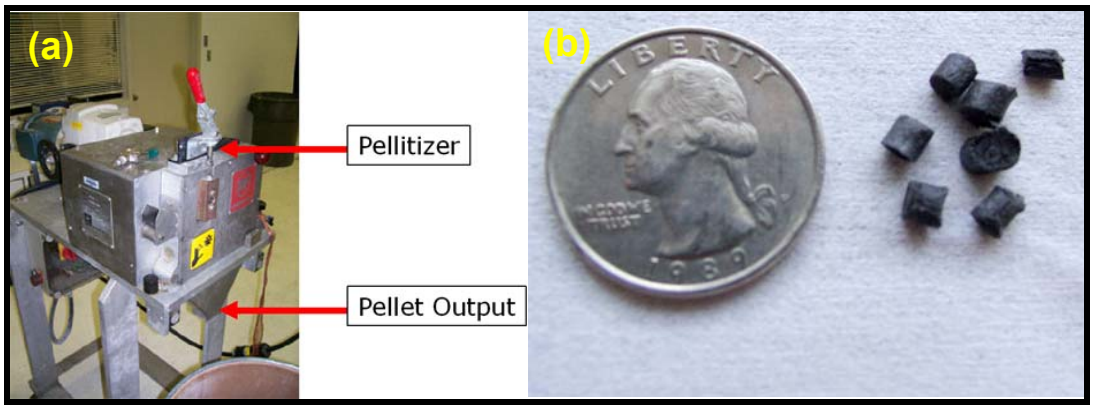

Figure 31 – (a) Pelletizer, (b) pellets formed from carbon fiber and polymer extrusion

Once the CFRP is pelletized, it is loaded into an injection molder. An example of an injection molding apparatus is shown in Figure 32a. A desired mold is used and the CFRP

material is heated to the required melting temperature. The molten material is then injected into the mold via a nozzle. Figure 32b shows mechanical test bars which were fabricated using injection molding.

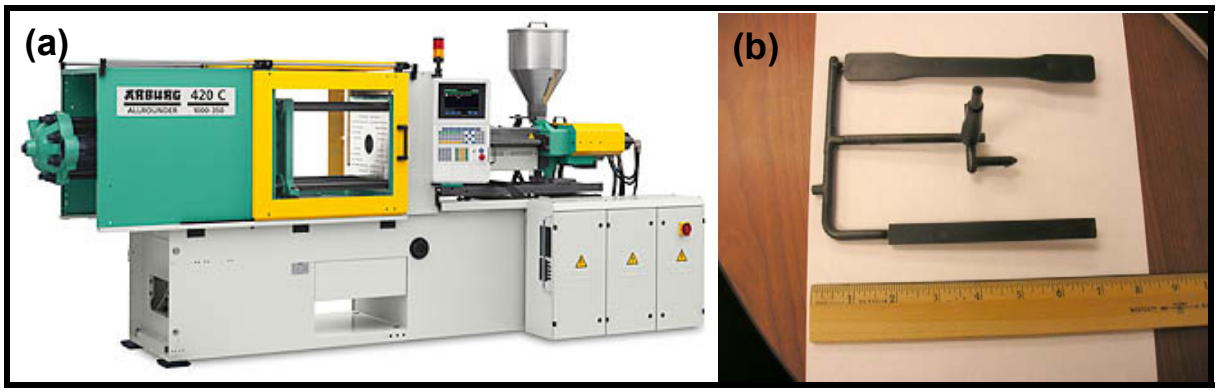

Figure 32 – (a) Injection molding machine, (b) CFRP test bars fabricated using injection molding

4. Issues Regarding Recycled Carbon Fiber

There are multiple issues regarding integration of recycled carbon fibers back into composites such as contamination of the fiber and fiber length distributions. Both EOL and manufacturing waste are affected by these issues which require engineering solutions to efficiently integrate recycled carbon fibers back into polymer matrices to produce consistently fabricated composites.

4.1 Contamination of Recycled Carbon Fiber

For recycling purposes, end-of-life composite scrap can contain high amounts of contamination. This type of contamination exists in the form of aluminum honeycomb core, copper wires, nuts, washers, bolts, and metal shards to name a few. Figure 33 shows bulky contamination found in EOL scrap. Finer contamination is also present and intermixed with

the fibers. Both bulky and fine contamination must be eliminated to avoid compromising the new composite's mechanical properties.

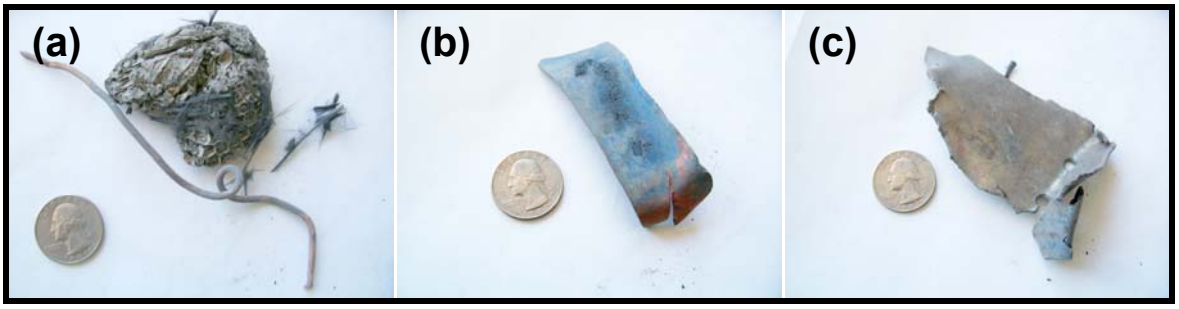

Figure 33 – Bulky contaminants found in carbon fiber supply derived from end-of-life composite scrap

Contamination is a serious problem, and new techniques need to leverage existing technologies to completely rid the fiber of contaminants. Figure 34 shows a vibrating mill at an inclined angle allowing contaminants to fall to the bottom of a sifting pan. Automation of this process would be a promising technology. Remnant contamination left on the fiber has the ability to seriously degrade the mechanical properties of the new composite by creating stress concentrators.

Figure 34 – The sequence of decontaminating CF (a) contaminants are vibrated towards the bottom of the pan, (b) contaminants are sorted in a bottom pan, (c) decontaminated CF

4.2 Recycled Carbon Fiber Size Distribution

The other main issue regarding the integration of RCFs into polymer matrices is the length distribution of the carbon fibers. In order to fabricate a consistent new composite part in the future, the recycled carbon fiber size distribution needs to be within certain tolerances, thus creating a reproducible part. The fiber, when reclaimed from composite materials, can have fibers ranging from about 1/8" to 12". The size distribution is an issue and fiber chopping mechanisms must be developed to cut the fiber to desired lengths. Typically when formulating a BMC or SMC, fibers of about ½" to 1" are used.

4.3 Conclusions

These aforementioned issues clearly need to be resolved before incorporating recycled carbon fibers back into polymer matrices. The technology for solving these problems is currently in its infancy and needs to be further developed. Fabricating a consistent part is crucial in industry, and issues with recycled carbon fibers need engineered solutions to aid in the construction of reproducible composite parts.

5. Previous Work Utilizing RCF Preforms / Integration of RCFs into Polymer Matrices

After supporting research concluded that recycled carbon fibers still retained their mechanical and surface properties, the next step is to introduce the reclaimed carbon fibers back into polymer matrices where little research has been completed. After recovery, RCFs are in mostly a random orientation. As a result, fiber preforms have been investigated to control the carbon fibers in a continuous preform material. This step is important because

virgin fibers are continuous and generated from a spool making them easy to use in composite manufacturing. Recycled carbon fibers are typically discontinuous and vary in length.

5.1 Aligned Recycled Carbon Fiber Mat

The University of Nottingham has fabricated an aligned fiber mat using recycled carbon fibers. The mat, shown in Figure 35a, is 1.5m x 0.13m. This work utilized fibers ranging from 5mm to 20mm. The electron micrograph in Figure 35b shows the alignment of the fiber mat. The fibers used to fabricate the preform were derived from the fluidized bed process.

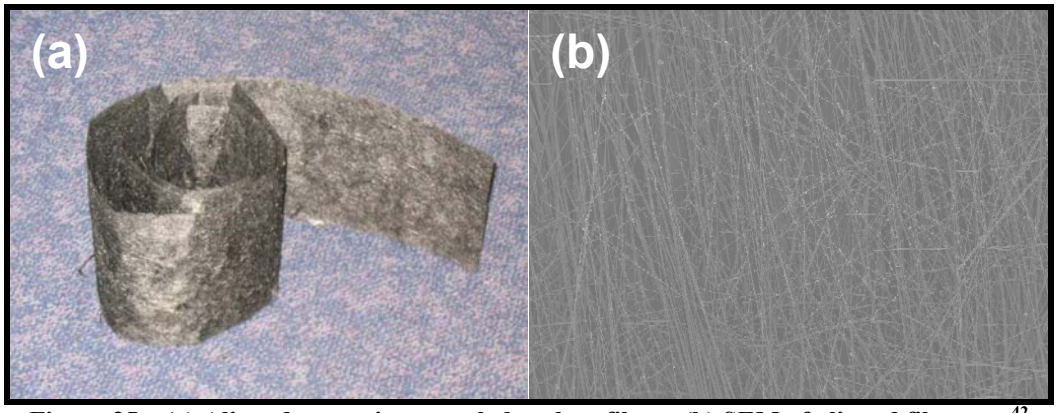

Figure 35 – (a) Aligned mat using recycled carbon fibers, (b) SEM of aligned fiber mat[42]

The fiber mat was fabricated using the apparatus shown in Figure 36a. Figure 36b shows the interior of the apparatus which essentially uses a slurry consisting of carbon fibers, drawing the slurry to the outside of the cylinder and causing the fiber to tangentially align to the walls of the cylinder.

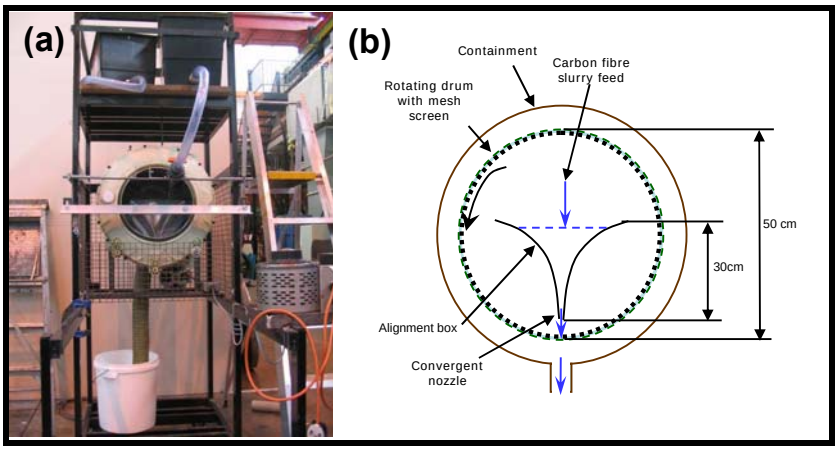

Figure 36 – (a) Apparatus used to fabricate the aligned fiber mat, (b) cross sectional schematic of the carbon fiber slurry and the cylindrical apparatus[42]

One technical obstacle to the fluidized bed process is the inability to process long fiber lengths efficiently (25mm) and maintain fiber lengths longer than 32mm. SMCs, being 40% RCF by volume, have the potential to replace glass prepreg. Figure 37a shows that a RCF SMC and BMC is more expensive than a glass prepreg (existing SMC and BMC). However, the RCF SMC and BMC demonstrate much greater mechanical strength compared to glass prepreg as seen in Figure 37b.[43]

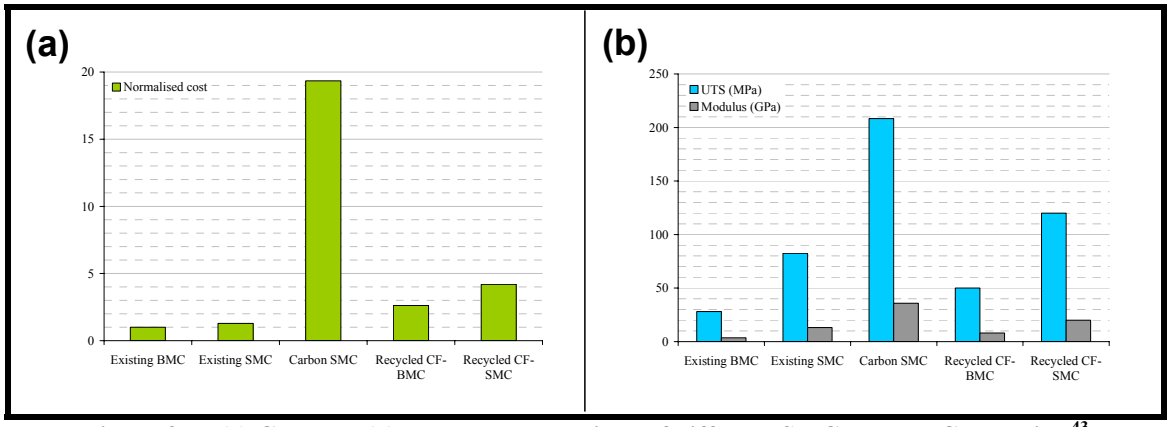

Figure 37 – (a) Cost and (b) strength comparison of different SMC and BMC materials[43]

5.2 Extrusion / Injection Molding

NC State, in collaboration with Boeing, was successful in extruding recycled carbon fibers with thermoplastic polycarbonate resin. The recycled fiber was obtained from Milled Carbon Ltd.'s continuous pyrolysis process. CFRP pellets, consisting of approximately 20 wt. % CF, were extruded and subsequently injection molded. Mechanical test bars were molded from the CFRP pellets and tested. The recycled carbon fiber filled polycarbonate was compared to an "off-the-shelf" commercial product line RTP 385. This CFRP consisted of virgin carbon fibers and a polycarbonate resin at the same loading percentage. The mechanical testing revealed the R-CFRP had quite comparable properties to the virgin filled material. The R-CFRP exhibited 12% decrease in tensile strength, 1.7% decrease in flexural strength, 3.2% decrease in notched Izod impact testing, and 26.3% increase in unnotched Izod impact testing. Figure 38 shows the injection molding sequence of the recycled carbon fiber filled polycarbonate producing mechanical test bars.[44]

Figure 38 – Recycled CF filled polycarbonate injection molding sequence

6. Characterization of Recycled Carbon Fibers from Air Force Composites

This research used characterization techniques to compare the surface and mechanical properties of recycled carbon fibers to virgin fibers. The characterization techniques

included TGA, SEM, XPS, and SFTT. When analyzing the RCFs, it was important to determine if the reclamation techniques had any negative effects on the fibers.

6.1 Test Materials

Cured composite panels were obtained from the Air Force for reclamation and analysis of the carbon fibers. A recycler, with a proprietary reclamation treatment and thermal techniques, reclaimed the carbon fibers. The code name of the CFRP material is A-03. This CFRP was originally comprised of unknown carbon fibers (not disclosed by the Air Force) and an epoxy resin, Huntsman RenInfusion 8606. Due to the Air Force not divulging the carbon fiber type, an AS4 virgin control fiber was used for comparison. The AS4 fiber is manufactured by Hexcel Corporation, and was chosen because it is an intermediate modulus carbon fiber.

6.2 Thermogravimetric Analysis

Thermogravimetric analysis was first performed on the A-03 CFRP to determine the temperature at which the composite started to experience weight loss. A Perkin Elmer TGA was used to conduct the experiment. This apparatus possesses the capability to reach 950˚C in temperature. The sample weighed approximately 10 mg and was exposed to a heating rate of 30˚C per minute in a nitrogen environment. A-03 was heated from 25˚C to 700˚C. After the test was complete, a derivative was developed from the original curve. This curve was analyzed to determine where the polymer started to decompose. This is expressed as the onset temperature. Figure 39 shows the TGA curve for the A-03 composite sample.

The A-03 CFRP originally contained an epoxy resin, and the results seemed to be consistent with when an epoxy composite tends to experience weight loss. The first onset temperature occurred at 343˚C and the peak occurred at 375˚C.

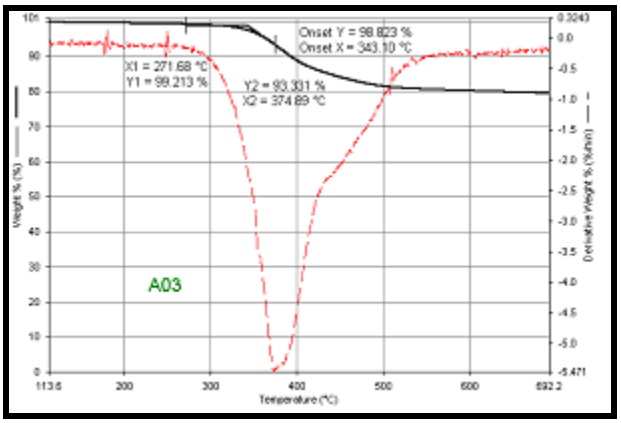

Figure 39 – TGA curve of A-03 original composite sample

6.3 Recycling Treatments of A-03 CFRP

The A-03 CFRP was exposed to a variety of reclamation treatments using a proprietary reclamation process and thermal treatments in order to determine which process produced the reclaimed carbon fibers with the best properties. These treatments are summarized in Table 2. The M4 sample was exposed to 4 minutes of a proprietary reclamation treatment reclaiming the carbon fibers from the composite material. M4+5 was exposed to 4 minutes of the reclamation treatment coupled with 5 minutes at 1000°C of air post treatment. The A2 sample received 2 minutes at 1000°C in an air muffle furnace. The A2+5 sample received 2 minutes at 1000°C in an air muffle furnace as well as 5 minutes at 1000°C of air post treatment.

Table 2 – Reclamation treatments of A-03 CFRP to reclaim carbon fibers

Sample	Reclamation Treatment	Air Muffle Furnace	Air Post Treat
AS4 Virgin Control	**--**	**--**	**--**
M4	4 minutes	--	--
M4 + 5	4 minutes	--	5 minutes
A2	--	2 minutes	--
A2 + 5	--	2 minutes	5 minutes

6.4 Scanning Electron Microscopy

Scanning electron microscopy was used to reveal the carbon fibers' surface morphology and properties at high magnifications. SEM uses an electron beam to strike the carbon fibers, resulting in the fibers emitting electrons. These emitted electrons are gathered by a detector and used to construct an image. The high resolution images help provide an understanding of what is occurring on the surface as well as understanding the morphology of the recycled fibers. The key observations to search for are surface damage to the fibers and residual resin present on the fibers after reclamation.

A Hitachi S-3200 variable pressure SEM was used to capture low magnification images from 250 to 4,000X. An accelerating voltage of 20 kV was used to examine the fibers. The samples were cut to approximately 5-10 mm^2 and mounted on an aluminum stub using double-sided carbon tape. All SEM analysis was conducted at the Analytical Instrumentation Facility (AIF) at NC State. Most importantly, it should be duly noted that these images are representative of the entire fiber sample set.

The AS4 virgin fiber was used as the control sample for the analysis. The fiber, shown in Figure 40, was very clean and contained few, if any, particulates on the surface. Although there was no sizing on the virgin fibers, some degree of orientation was present.

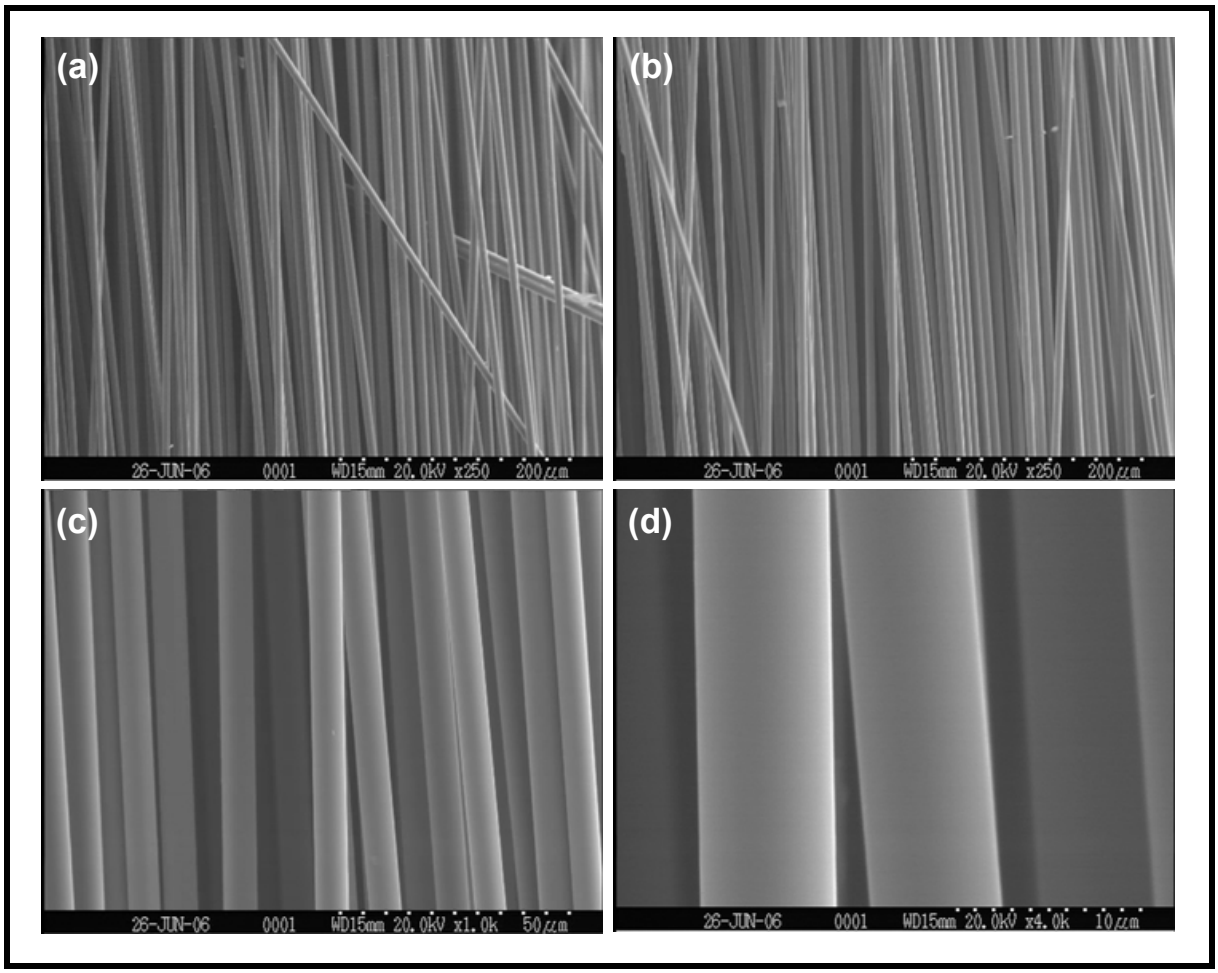

Figure 40 – SEM micrographs of AS4 virgin carbon fiber control sample at (a) 250X, (b) 250X, (c) 1,000X, (d) 4,000X

The RCFs derived from the CFRP which experienced 4 minutes of a reclamation treatment (M4) still contained considerable amounts of resin and carbonaceous char on the surface which made the sample stiff. In Figure 41c, there are considerable amounts of resin still adhering to the fibers, holding them together. The reclamation technique did not remove all the resin from the A-03 composite using this treatment. Discrepancies exist between micrographs Figure 41a and Figure 41b. Figure 41a does not reveal as much resin or char on the surface of the fibers compared to Figure 41b. Both types of behavior were present and documented as representative images of the recycled carbon fibers.

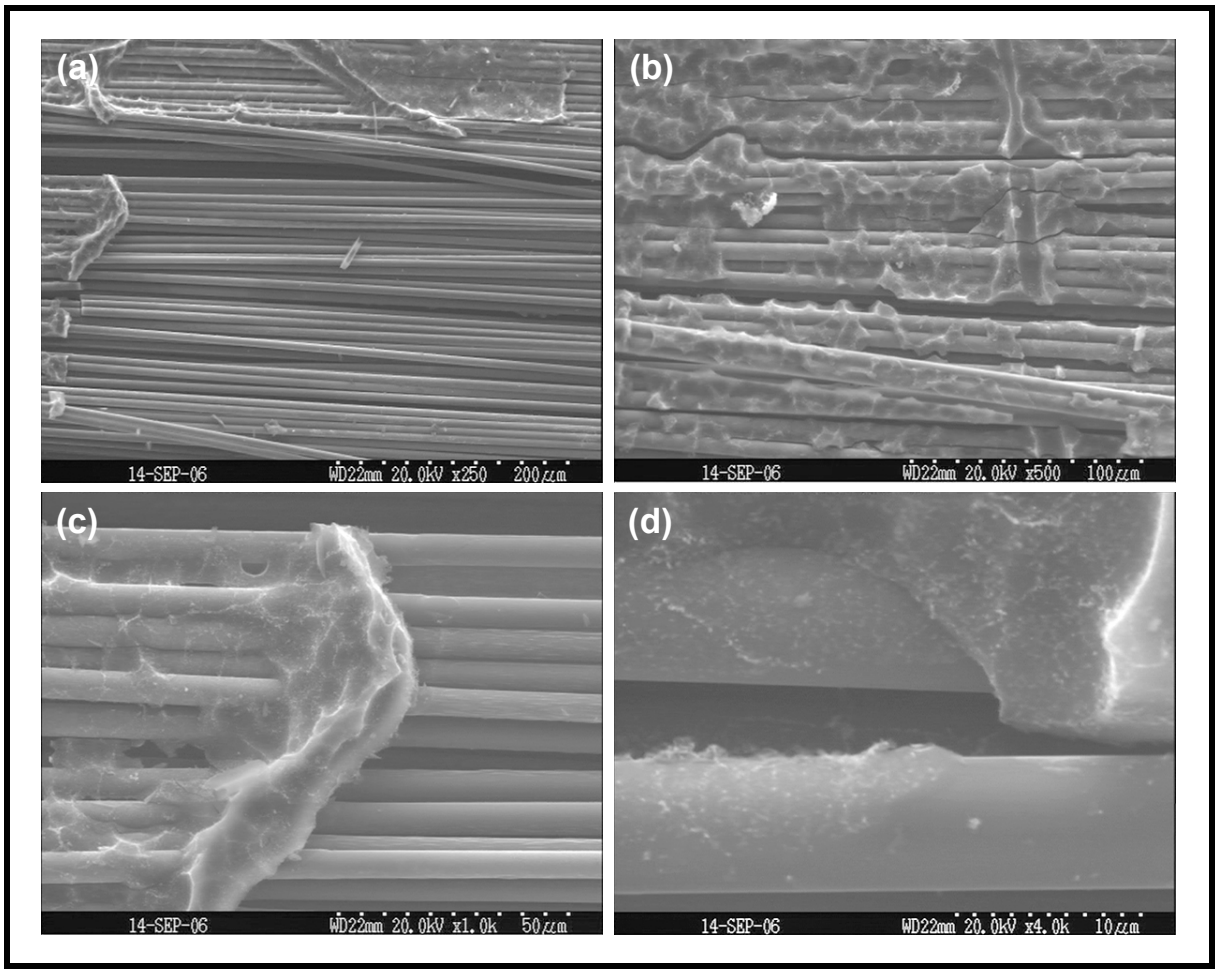

Figure 41 – SEM micrographs of M4 recycled carbon fiber at (a) 250X, (b) 500X, (c) 1,000X, (d) 4,000X

The second CFRP sample received 4 minutes of the reclamation treatment as well as 5 minutes of air treatment at 1000°C (M4+5). The fibers are shown in Figure 42. A considerable difference in the fiber surfaces exists when comparing M4 to M4+5. M4+5 has considerably lower amounts of carbonaceous char as well as less resin still present on the surface of the fibers. The 5 minutes of thermal treatment in air at 1000°C helped remove the remnant resin. Few particulates are present on the surface of the fibers which looks promising.

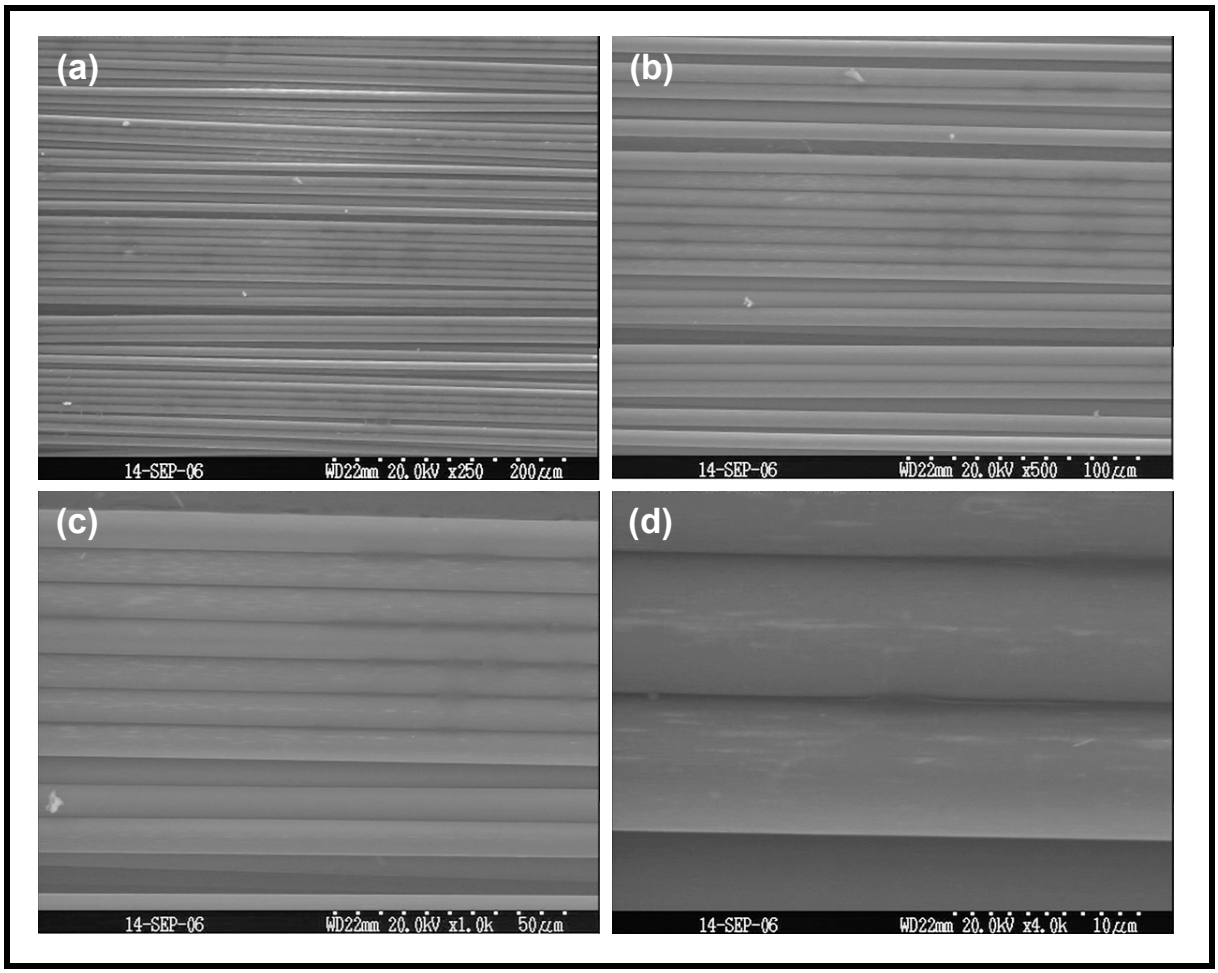

Figure 42 – SEM micrographs of M4+5 recycled carbon fiber at (a) 250X, (b) 500X, (c) 1,000X, (d) 4,000X

A2 was the next sample analyzed using the variable pressure SEM. Here, A-03 CFRP was subjected to 2 minutes at 1000°C in an air muffle furnace to free the carbon fibers. As shown in Figure 43, A2 exhibited similar surface characteristics to M4+5. The RCF surfaces were relatively clean and still exhibited some form of orientation. Slightly more particulates were present on A2 compared to the AS4 virgin control fiber.

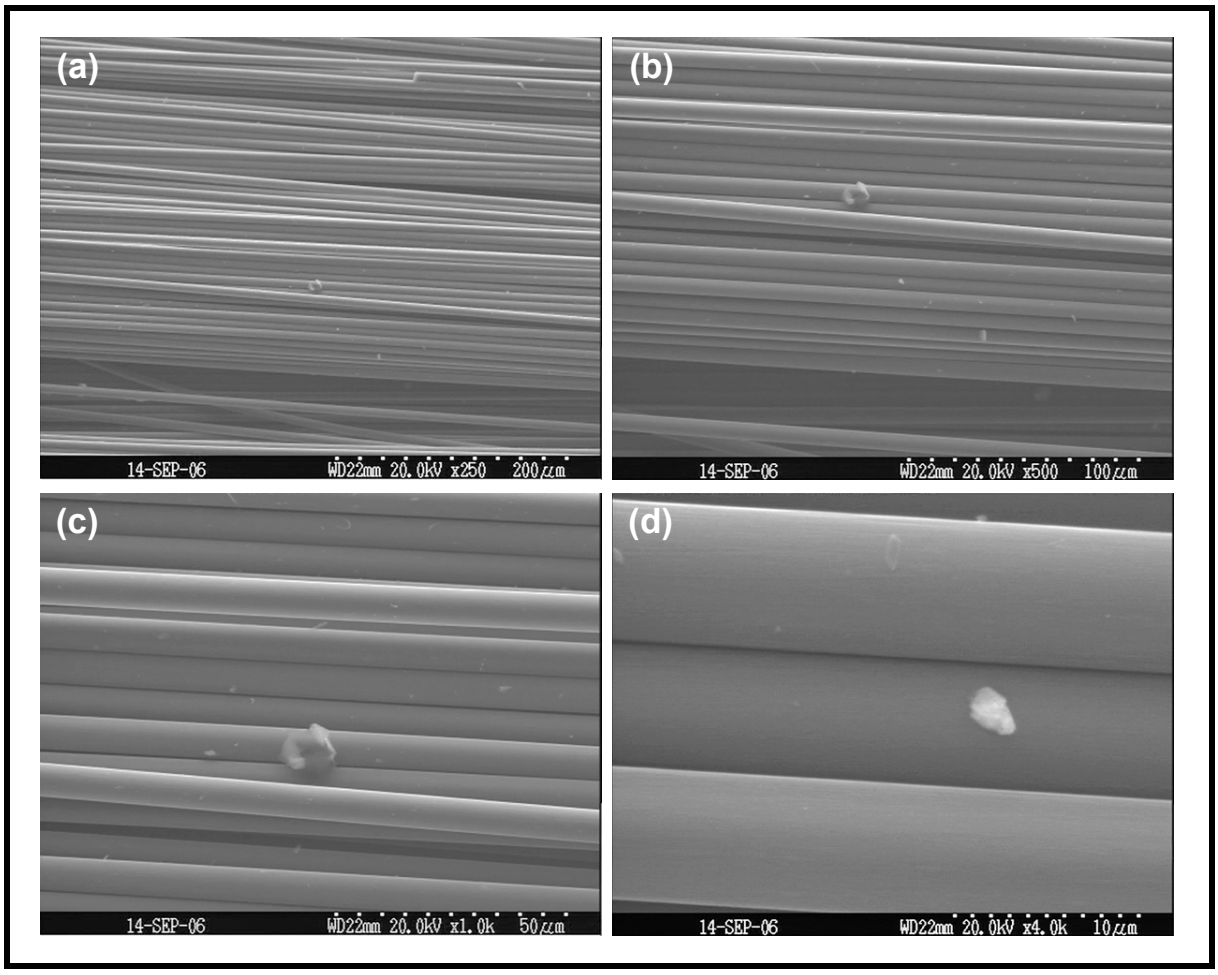

Figure 43 – SEM micrographs of A2 recycled carbon fiber at (a) 250X, (b) 500X, (c) 1,000X, (d) 4,000X

The A2+5 fibers, shown in Figure 44, exhibited very similar surface characteristics to A2. Here, the A-03 composite experienced 2 minutes at 1000°C in an air muffle furnace and an additional treatment of 5 minutes at 1000°C in air. Comparing micrographs of A2 and A2+5, it seems the extra 5 minutes at 1000°C in air is not necessary to remove the resin from the fibers. A2+5 fibers still retained somewhat aligned fibers and had few particulates present on the surface. Also, in Figure 44a a few fractured fibers are present.

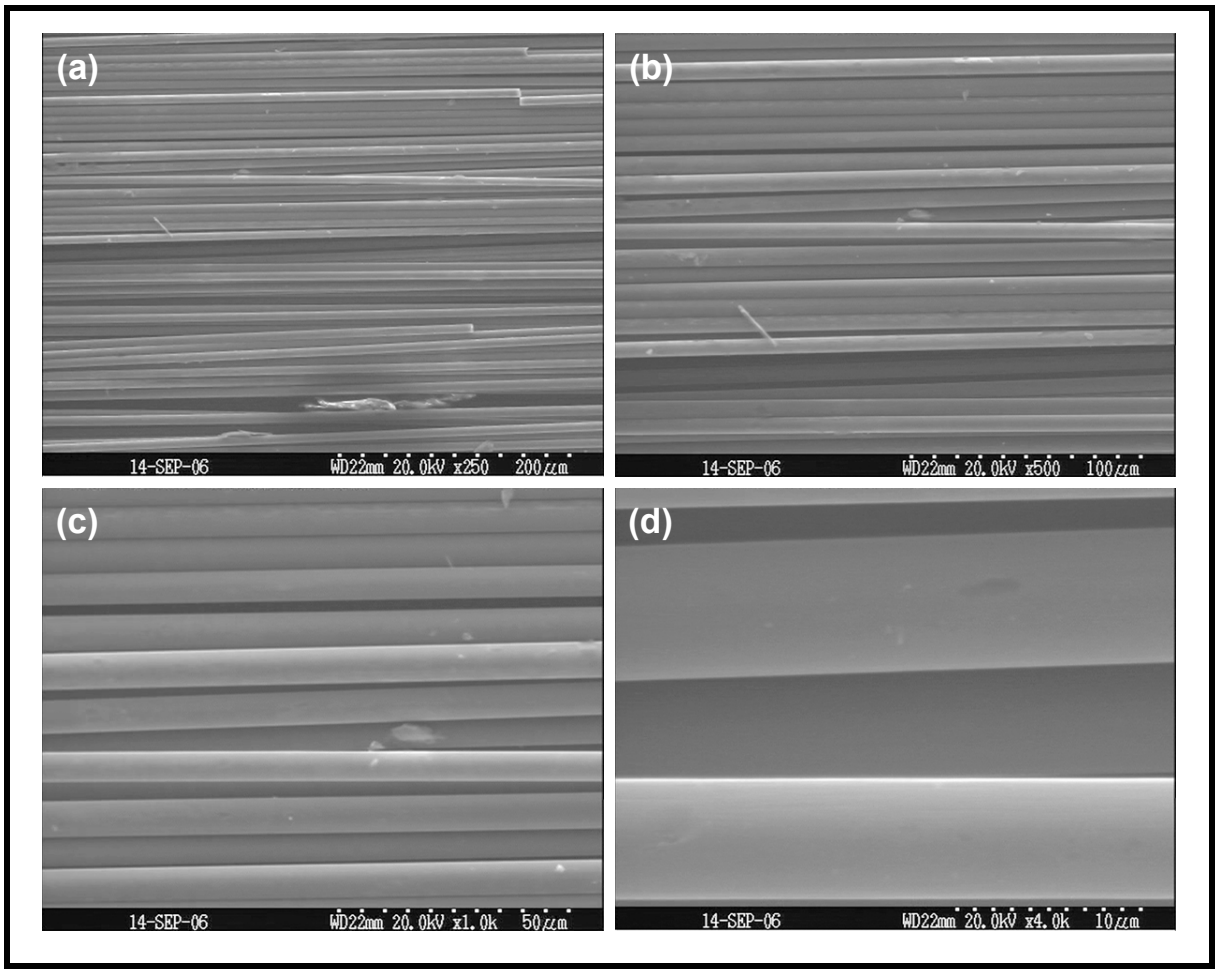

Figure 44 – SEM micrographs of A2+5 recycled carbon fiber (a) 250X, (b) 500X, (c) 1,000X, (d) 4,000X

Overall, no real structural damage to the carbon fibers was caused by the reclamation techniques. The M4 carbon fibers clearly contained a considerable amount of resin and carbonaceous char present on the surface compared to all other fibers analyzed. Particulates were present on all of the reclaimed fiber samples as well. Three treatments (M4+5, A2, and A2+5) left fiber surfaces comparable the AS4 virgin fibers. All fiber sets had some form of orientation as well.

6.5 Single Fiber Tensile Testing

To determine the mechanical properties of single filaments, single fiber tensile testing was performed on the control fiber and the three recycled fibers. Testing the mechanical strength of the recycled fibers is important to determine if the reclamation techniques had any severe effects on the strength of the fibers.

Each of the test specimens were mounted on note cards with a gauge length of 1 inch and pulled to failure using an MTS Sintech universal tensile testing machine. Figure 45 shows how an individual fiber was mounted on an index card and inserted into the tensile testing apparatus. Acrylic adhesive and tape were used to secure the fiber ends to the note card. After loading the sample in the grips, the note card was cut along the dotted line shown in Figure 45a. This placed the entire load on the fiber.

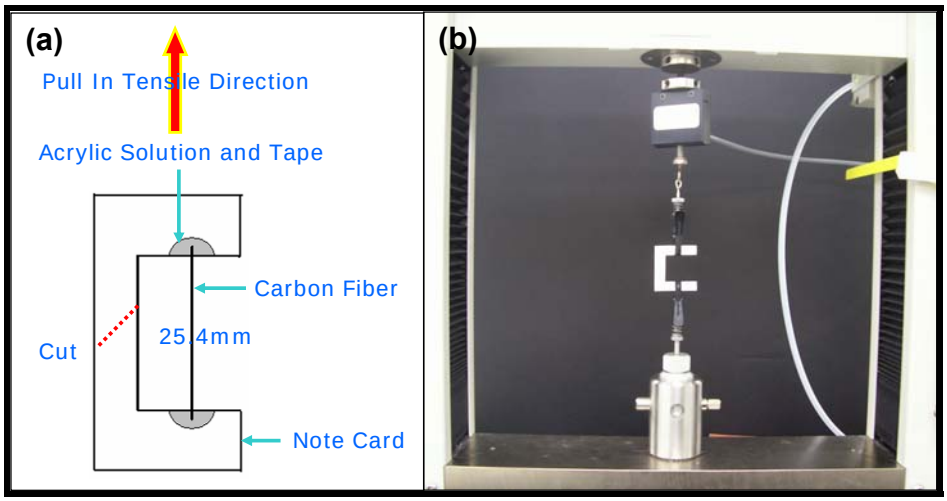

Figure 45 – (a) Single carbon fiber test specimen mounted on note card, (b) note card with fiber mounted in tensile testing apparatus

The Japanese Industrial Standard, JIS R 7601 for single fiber tensile testing, was followed as a guide for testing procedures. A 50 g load cell was used as well as a strain rate

of 10 mm/min. At least 12 specimens were tested per sample set. Load versus elongation was plotted and then converted into ultimate tensile strength (UTS), fiber modulus, and percent elongation.

Assuming cylindrical geometry of the fibers, the cross sectional area was calculated using equation 1 below. The diameter of the fiber is represented by d. SEM micrographs were used to determine the diameter of the fibers.

$$A = \frac{\pi d^2}{4} \qquad [1]$$

Denier measurements were also determined for each sample using equation 2. It was assumed the density (ρ) of the fiber was 1.79 g/cm^3. This is the density value reported in the AS4 technical data sheet.

$$\text{Denier} = \rho \cdot A = 1.79 \cdot \frac{\pi d^2}{4} \cdot 9 \times 10^{-3} \ \ {}^{g}\!/_{9000m} \qquad [2]$$

Table 3 shows the data compiled from the testing. Another reference fiber from Hexcel, virgin IM7, was used for comparative purposes as well. This fiber will be used later as the virgin fiber reinforcement for VARTM fabricated panels. The numbers in parentheses represent the standard deviation of the data. This nomenclature will be used throughout this work. To better compare the different mechanical properties, bar graphs summarized the data in Figure 46 through Figure 49.

Table 3 – Mechanical properties of RCF derived from A-03 CFRP compared to the virgin control AS4 fiber by single fiber tensile testing

Property / Fiber	Virgin AS4	M4	M4+5	A2	A2+5	Virgin IM7
Avg. UTS [GPa]	3.80 (0.87)	2.80 (1.17)	1.99 (0.19)	2.51 (0.12)	1.34 (0.28)	6.86 (3.52)
Avg. Fiber Modulus [GPa]	225 (59)	214 (40)	192 (15)	198 (52)	219 (79)	364 (257)
Avg. Percent Elongation [%]	2.20 (0.40)	1.44 (0.34)	0.79 (0.30)	1.21 (0.90)	1.31 (0.29)	2.45 (0.55)
Avg. Fiber Diameter [µm]	7.37 (0.06)	7.21 (0.22)	7.39 (0.09)	7.41 (0.14)	7.31 (0.05)	4.92 (0.28)
Denier	0.688	0.659	0.692	0.696	0.677	0.303

Figure 46 shows the average ultimate tensile strength of the four recycled fibers was lower than the virgin AS4 fiber. M4 retained 74% of the ultimate tensile strength, which was the highest strength retention of the four treated samples. A2+5 has the greatest ultimate tensile strength degradation, only retaining 35% UTS compared to the virgin AS4 control. This could be attributed to the extra 5 minutes of treatment degrading the fiber's strength.

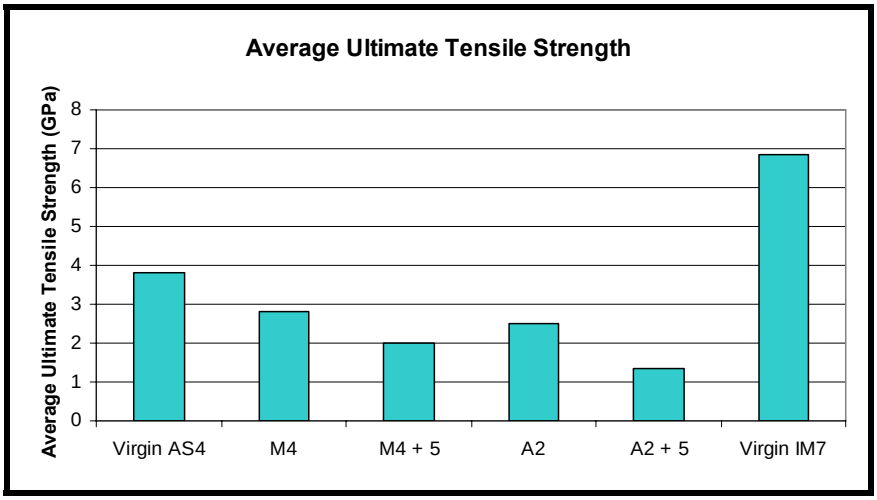

Figure 46 – Average ultimate tensile strength of the A-03 fiber set compared to the virgin AS4 fiber in a single fiber tensile test

The AS4 technical data sheet reports an ultimate tensile strength of 4.48 GPa, whereas the experimental testing revealed an ultimate tensile strength of 3.80 GPa. There is a 15% difference in the manufacturer's data and our experimental data. However, this discrepancy can be linked to the gauge length used during testing. Typically the ultimate tensile strength of the fiber increases as the gauge length decreases. Hexcel could have used a gauge length as small as 5 mm to perform the testing.

Fiber modulus is one of the most important mechanical properties used to classify the strength of carbon fibers. Fibers are normally classified as ultra-high, high, intermediate, and low modulus carbon fibers. Figure 47 shows the fiber modulus was not drastically degraded by the four treatments. All four RCFs contained very similar elastic moduli compared to the virgin fiber (85%-97% retention). This could be attributed to not all resin being removed from the fibers, therefore causing the RCFs to have more stiffness. M4 clearly showed resin still present on its surface.

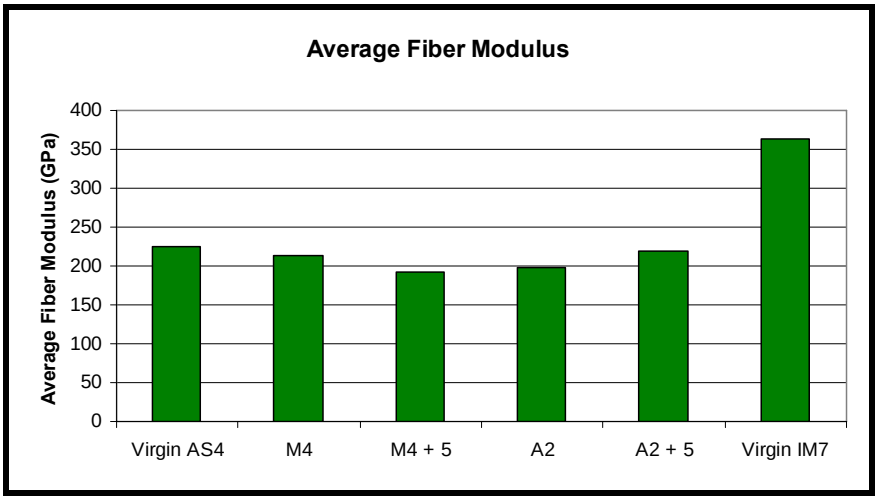

Figure 47 – Average fiber modulus of the A-03 fiber set compared to the virgin AS4 fiber in a single fiber tensile test

Hexcel reported an elastic modulus of 231 GPa for the AS4 fiber in the technical data sheet. Our experimental data shows an elastic modulus of 225 GPa. These two values are quite close to one another. With the experimental procedure remaining constant for all specimens tested, it appears the testing procedure is providing data with a high degree of confidence as compared to the manufacturer's data.

The four RCFs did not elongate as much as the virgin AS4 fiber as shown in Figure 48. M4 retained 65% of the elongation compared to the virgin AS4 fiber. M4+5 performed the poorest, retaining only 36% of its average elongation compared to that of the virgin fiber.

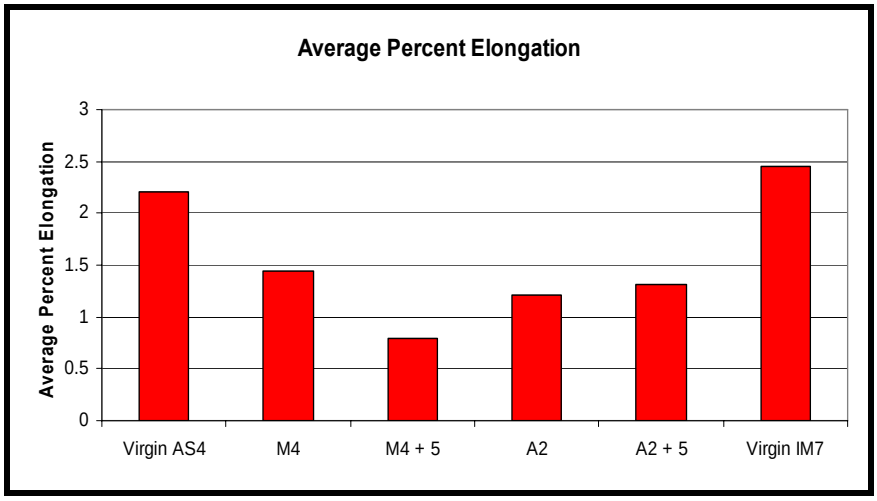

Figure 48 – Average percent elongation of the A-03 fiber set compared to the virgin AS4 fiber in a single fiber tensile test

The AS4 virgin fiber actually outperformed the manufacturer's data with respect to percent elongation. Hexcel reported an average percent elongation of 1.8%, whereas our experimental data showed an elongation of 2.2%. However, these numbers are quite comparable.

The average single fiber diameters, shown in Figure 49, were found using SEM micrographs. The AS4 fiber was used as a control fiber, and was not necessarily the same fiber reinforcing the A-03 CFRP. The AS4 virgin fiber contained a measured average fiber diameter of 7.37 μm. Hexcel reports the fiber diameter of 7.1 μm which is close to the fiber diameter measured. The reclaimed fibers' diameters are very close to the virgin fiber's diameter, indicating the possibility the RCFs are in fact AS4 type fiber.

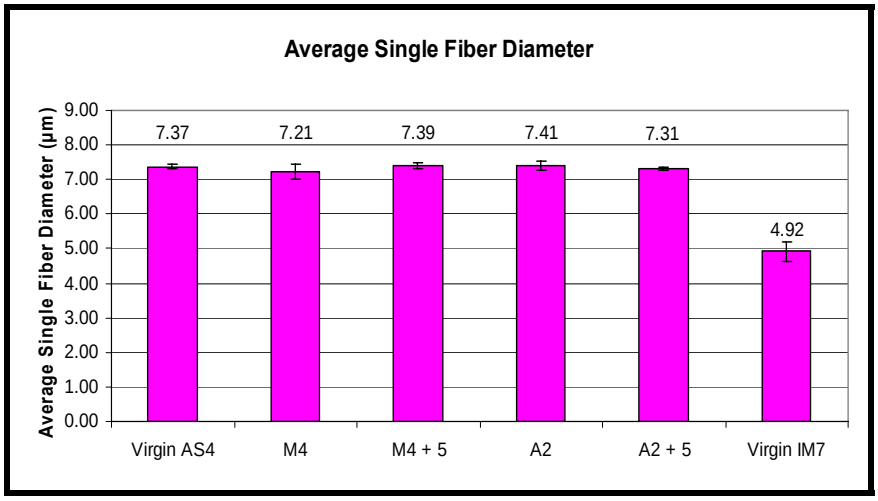

Figure 49 – Average single fiber diameter of the A-03 fiber set compared to the virgin AS4 control sample

6.6 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy, also called Electron Spectroscopy for Chemical Analysis (ESCA), uses x-rays to eject electrons from the inner-shell orbitals of specimens. XPS is a surface analysis technique providing elemental information of layers up to 3 nm thick. The emitted electrons are used to characterize the surface chemistry of the carbon fibers. A Riber XPS system was used to conduct this analysis at AIF.

The overall XPS scan is used to determine the relative percentage of elements present

on the surface of the carbon fibers including carbon, oxygen, and nitrogen. XPS is also used to resolve different types of chemical bonds between elements. In this research, a specific section of the C 1s peak is chosen for deconvloution. Known bonding curves such as C-C (graphitic), C-O (hydroxyl), C=O (carbonyl) and O-C=O (carboxylic acid) functional groups are then superimposed onto this large carbon curve. These curves are formed using XPS data of known elemental bonding or extracted from XPS analysis literature. These known bonding curves are used to determine the percentages of the carbon/oxygen bond types present.

The overall atomic percentages on the surface of the virgin control fiber as well as the four recycled carbon fibers were found. Table 4 reveals the data collected. The RCFs seemed very consistent with one another with no drastic differences between the samples. Also, the reclaimed carbon fibers were somewhat comparable to the AS4 virgin control fiber. The AS4 virgin control sample did not contain any Na on the surface, whereas all reclaimed carbon fibers did. Figure 50 uses a bar graph for comparing the different atomic percentages found on the surface of the carbon fibers. It is promising to see the reclaimed carbon fibers have similar surface chemistry to a virgin fiber. However, the AS4 control fiber had a somewhat higher oxygen concentration on the surface compared to the RCFs. This will be revealed in more detail in the deconvolution data.

Table 4 – XPS data revealing the overall atomic percentages on the surface of the fibers

Element / Sample	AS4 Virgin Control	M4	M4+5	A2	A2+5
C 1s	83.14	82.23	82.55	83.84	81.38
O 1s	14.28	11.54	11.54	11.47	12.86
N 1s	2.58	4.83	3.93	2.54	3.13
Na 1s	--	1.40	1.98	2.14	2.63

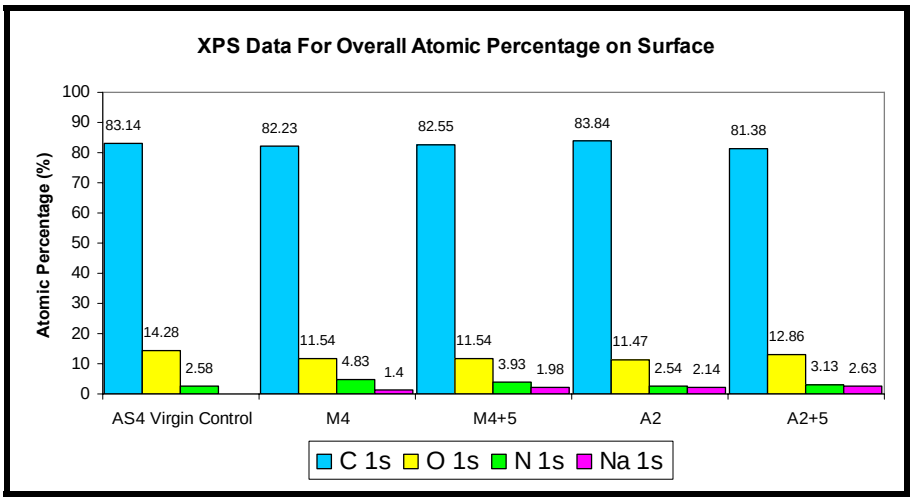

Figure 50 – XPS data revealing the overall atomic percentages on the surface of the carbon fibers

Throughout literature, ratios of elements present on the surface of the fibers are commonly presented using the overall atomic percentages. Typically, the O/C, N/C and (O+N)/C ratios are calculated. This information helps to show if there are considerable contributions of oxygen present on the surface. Literature indicates the larger the percentage of oxygen containing functional groups present, the better fiber to resin adhesion.[45,46] Table 5 summarizes the ratios derived from the overall atomic scan of the carbon fiber surfaces.

Table 5 – Atomic ratios derived from the XPS overall atomic percentage scan of the CF surfaces

Ratio / Fiber	AS4 Virgin Control	M4	M4+5	A2	A2+5
O/C	0.172	0.140	0.140	0.137	0.158
N/C	0.031	0.059	0.048	0.030	0.038
(O+N)/C	0.203	0.199	0.187	0.167	0.196

The table shows that A2+5 has the closest O/C ratio compared to the AS4 virgin control sample. This might be expected due to the extra oxidative treatment the CFRP experienced to reclaim the fibers. The other three reclaimed carbon fibers exhibited similar

O/C ratios compared to one another, yet were not very similar to the virgin fiber's (0.172).

Figure 51 through Figure 55 shows the XPS data collected for the carbon fiber samples. The overall scan is shown in Figure Xa and the deconvolution of the carbon peak is shown in Figure Xb. The carbon peak occurs in the scan around 285 eV.

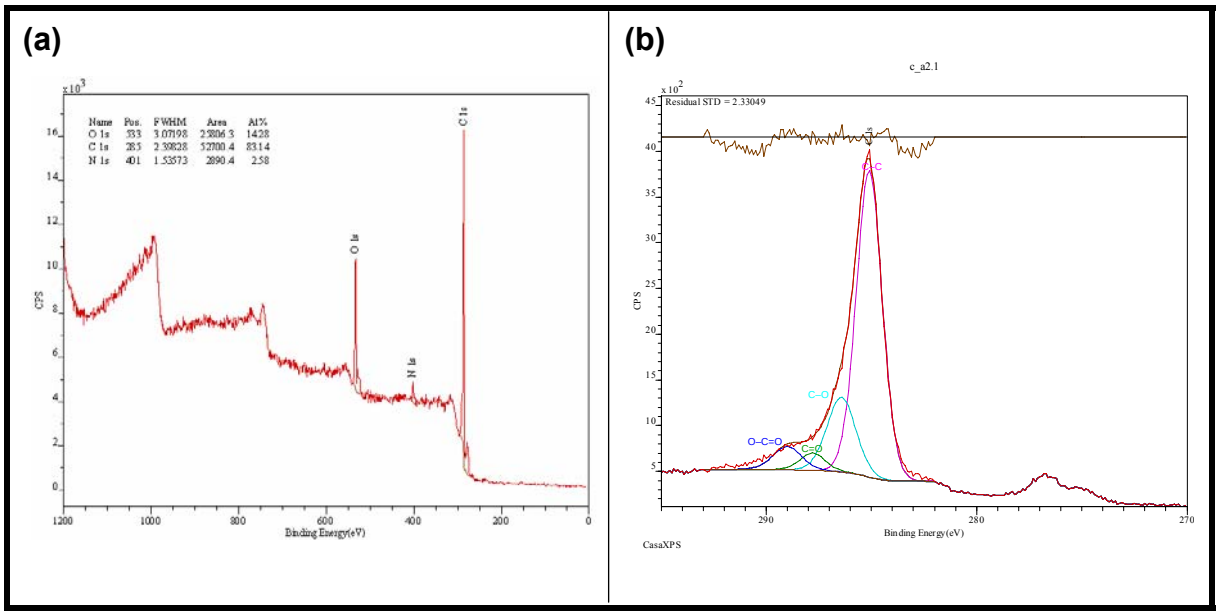

Figure 51 – AS4 virgin fiber control (a) XPS overall scan for atomic percentages on the surface, (b) deconvolution of carbon peak revealing the functionalities of the carbon peak

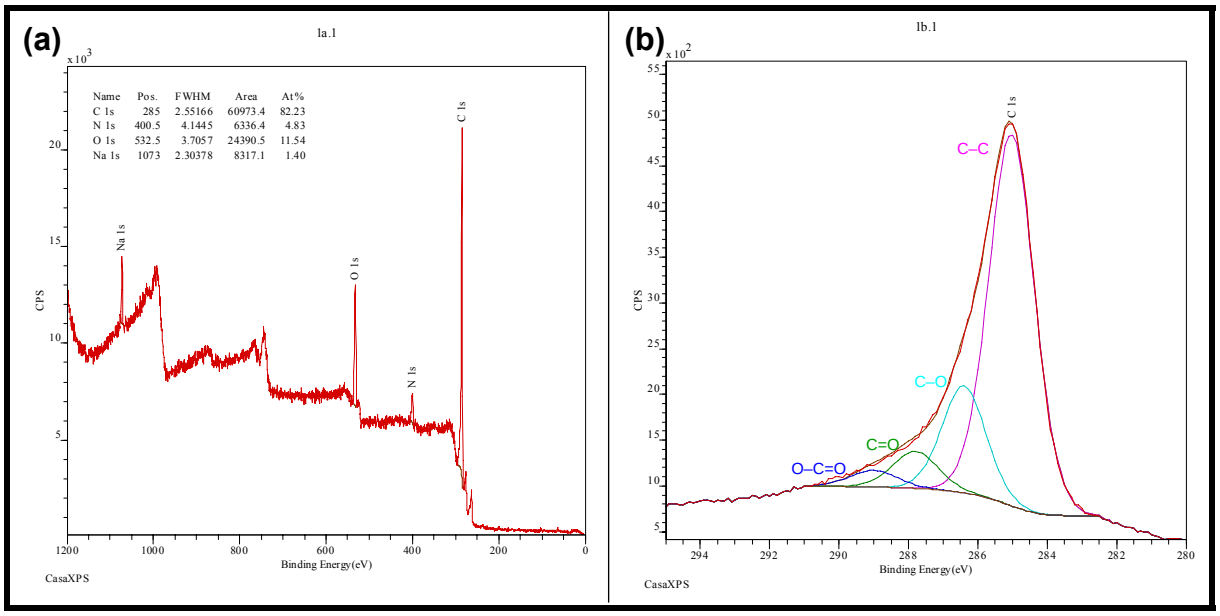

Figure 52 – M4 (a) XPS overall scan for atomic percentages on the surface, (b) deconvolution of carbon peak revealing the functionalities of the carbon peak

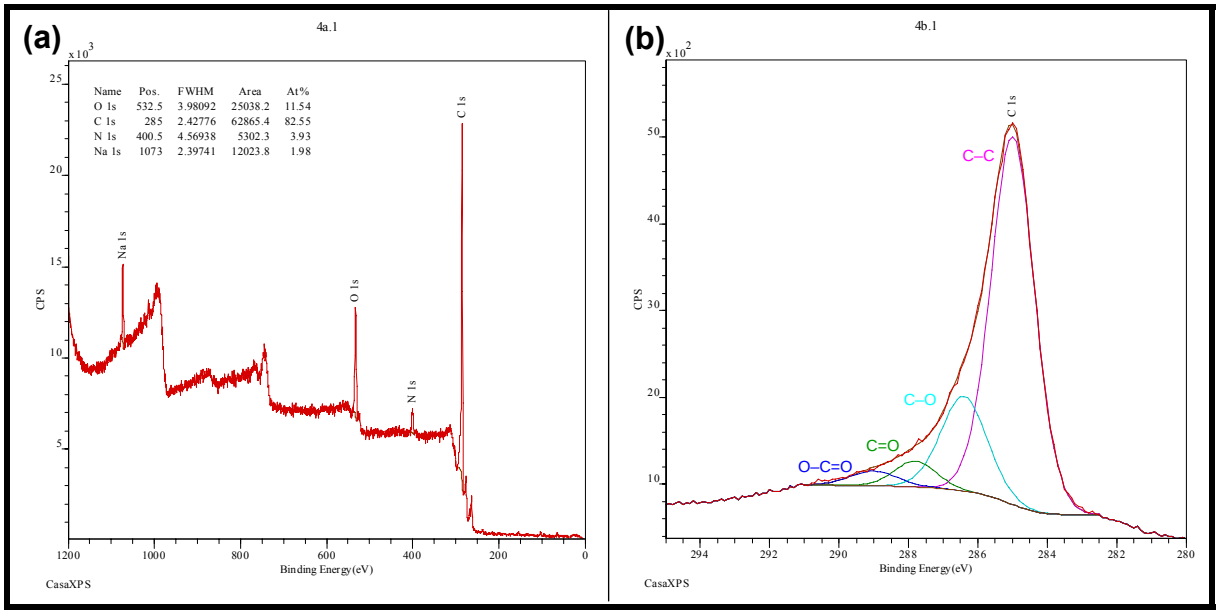

Figure 53 – M4+5 (a) XPS overall scan for atomic percentages on the surface, (b) deconvolution of carbon peak revealing the functionalities of the carbon peak

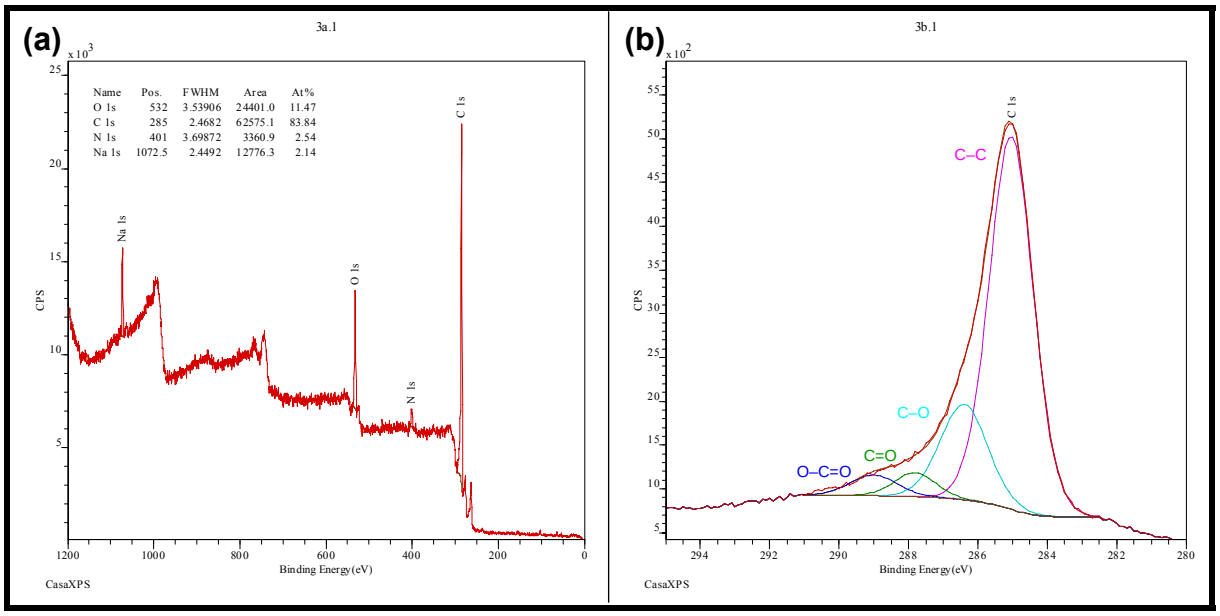

Figure 54 – A2 (a) XPS overall scan for atomic percentages on the surface, (b) deconvolution of carbon peak revealing the functionalities of the carbon peak

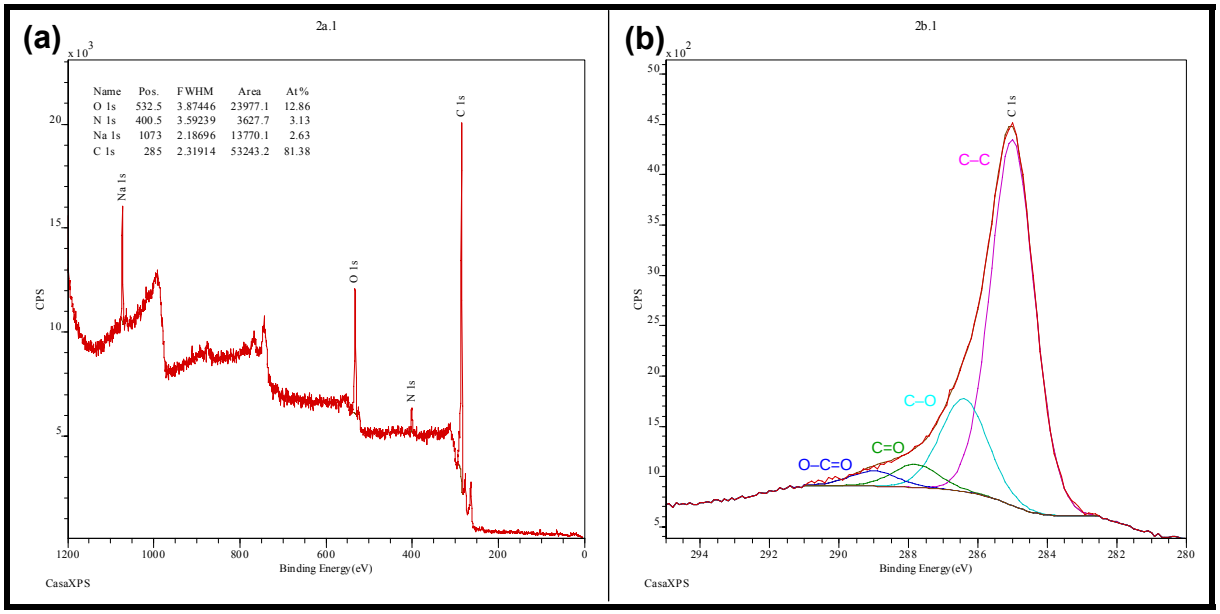

Figure 55 – A2+5 (a) XPS overall scan for atomic percentages on the surface, (b) deconvolution of carbon peak revealing the functionalities of the carbon peak

The deconvolution of the carbon peak helps show how the carbon atoms are bonding on the surface of the fiber. By deconvlouting the carbon peak, the different functional groups

on the surface of the fibers can be found. The breakdown of the different functional groups is shown in Table 6. Figure 56 also shows a bar graph for comparative purposes.

Table 6 – Percent functionality of the carbon peak via XPS deconvolution of C 1s peak

Sample / Bonding	C-C (Graphitic)	C-O (Hydroxyl)	C=O (Carbonyl)	O-C=O (Carboxylic Acid)
AS4 Virgin Control	70.65	19.38	3.93	6.04
M4	70.34	19.44	6.96	3.26
M4+5	72.22	19.74	4.88	3.16
A2	71.7	19.68	4.36	4.26
A2+5	72.05	19.83	4.86	3.26

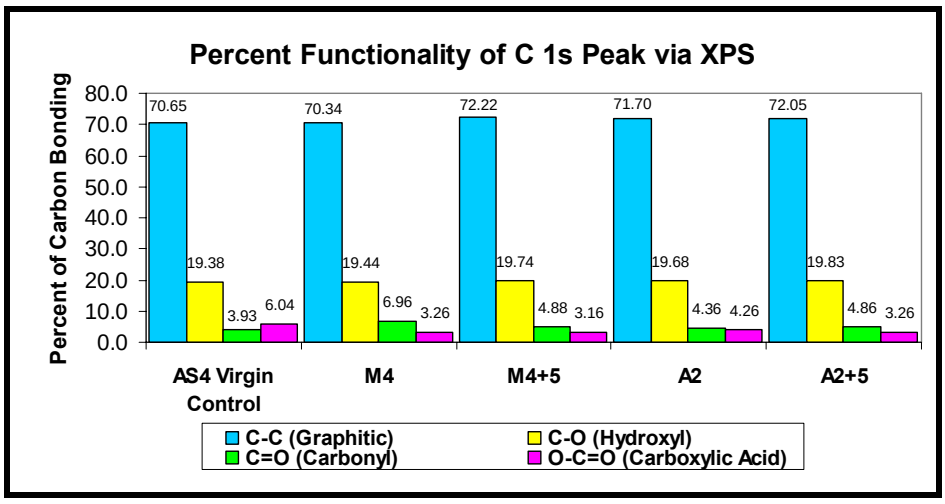

Figure 56 – Percent functionality of C 1s peak via XPS data for the carbon fiber samples

The data shows that virgin AS4 carbon fiber had a considerably higher carboxylic acid bonding on its surface compared to the RCFs. The hydroxyl bonding was virtually identical for all samples. M4 contained a large percentage of C=O bonding which could be attributed to resin still on the fibers.

6.7 Conclusions

Characterization of the RCFs reclaimed by various techniques yielded fibers which were comparable to virgin AS4 fiber in many regards. The fibers did not exhibit quite the amount of ultimate tensile strength the virgin AS4 control fiber showed (35%-74% retention). This could be attributed to the vigor of the reclamation techniques, especially at elevated temperatures (1000°C in an environment consisting of air). However, the decrease in ultimate tensile strength was not drastic for M4 which retained 74% UTS. In addition, the RCFs had similar elastic moduli compared to the AS4 virgin fiber.

The scanning electron micrographs revealed the recycled carbon fibers did not show signs of serious surface damage due to the reclamation techniques. There were few if any surface defects present on the carbon fibers. The SEM micrographs also revealed the resin was not completely removed from the M4 fibers. The other fibers contained a few particulates but were quite comparable to the virgin AS4 fibers.

The XPS data showed the AS4 virgin fiber had a higher oxygen percentage on the surface than the RCFs. M4 clearly contained resin still on the surface of the fiber as confirmed by a large percentage of the C=O carbonyl bond. The rest of the RCFs, when compared to the virgin AS4 fiber, had very similar functionalities, which is quite promising.

Thus, the characterization techniques used to analyze the fibers found promising surface and mechanical properties compared to their virgin counterparts. The variations of the reclamation techniques yielded fibers which could then be introduced into a variety of different resins.

7. Integration of Recycled Carbon Fibers into New Polymer Matrices

Recycled carbon fibers were integrated into new polymer matrices in a variety of ways all of which are fabrication techniques currently used to manufacture composites. VARTM, BMC, and compression molding are the techniques used in this research to reintroduce recycled carbon fibers back into composites. Different types of recycled fibers were used (milled and chopped) in various combinations with thermoset resins (epoxies, vinyl esters, and phenolics). The mechanical properties of the cured composites were found using an array of mechanical tests. Furthermore, a 3-D fuse box panel cover, consisting of RCF reinforcement, was fabricated using a bulk molding compound. This proved that recycled carbon fibers could actually be used to make a functional part.

Table 7 illustrates the fabrication techniques used in this research to create composites utilizing reclaimed fibers. The original composite constituents (fiber and resin) are shown along with the new resin for fabricating the RCFs and the control fiber used for comparative purposes. The newly formed composite was exposed to the mechanical tests in the last column. It should be noted that the reclaimed AS4 fibers used in compression molding sets #1 and #2 and the BMC trials were previously characterized by NC State and derived from Milled Carbon Ltd.'s continuous pyrolysis process.

Table 7 – Overview of the original constituents of the composite deriving carbon fibers for reintroduction into new resin systems and mechanical testing of the newly formed composites by different techniques

Fabrication Technique	Original Fiber	Original Resin	New Resin	Control Fiber	Mechanical Tests Performed
VARTM Set #1	Not Disclosed	Huntsman 8606 Epoxy	EPON 862 + W Catalyst	Sized IM7	Tensile, Compression, ILSS
VARTM Set #2	IM7	EPON 862 + W Catalyst	EPON 862 + W Catalyst	Sized IM7	Tensile, Compression
Compression Molding Set #1	AS4 (MC) / Not Disclosed (MB2+5)	Hexcel 3501-6 Epoxy (MC) / Huntsman 8606 (MB2+5)	EPON 862 + W Catalyst	Not Used	Tensile, Flexure, Compression
Compression Molding Set #2	AS4	Hexcel 3501-6 Epoxy	EPON 862, 9504, 826	Not Used	Tensile, Compression
BMC Plaque Fabrication (BMCI)	Milled AS4	Hexcel 3501-6 Epoxy	Vinyl Ester 8581	Asbury MF-0150	Tensile, Flexure
BMC 3-D Part Fabrication	Milled AS4	Hexcel 3501-6 Epoxy	Plenco 14399 Phenolic	Not Used	Not Tested

7.1 VARTM Fabrication Technique

Two sets of recycled carbon reinforced plastic panels were fabricated using the VARTM technique which infuses resin amongst the fibers with the assistance of a vacuum pull. Figure 57 shows the setup used to create the test panels. North Carolina A&T State University was vital to the production of the composite panels.

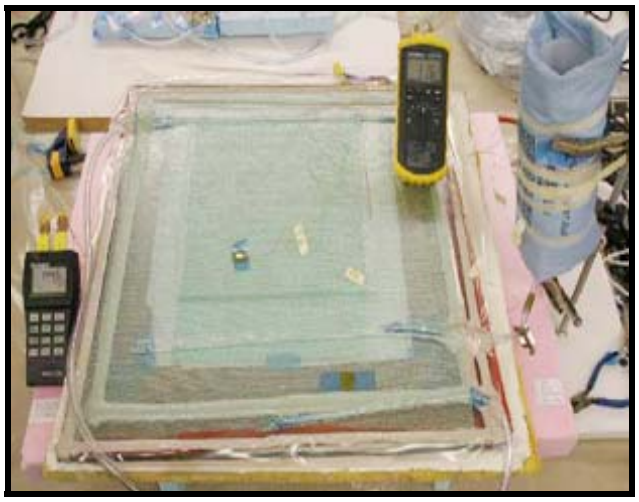

Figure 57 – Vacuum Assisted Resin Transfer Molding setup

Virgin carbon fiber reinforced control panels (12" x 12") were fabricated from 10 fabric layers consisting of plain weave general purpose sized IM7 balanced tow (11 tows in weft and warp directions). The control fiber used in the SFTT was AS4, and the control fiber used for composite fabrication is sized high modulus IM7. However, the virgin IM7 fiber was also tested in parallel in the SFTT trials for comparative purposes. The IM7 virgin fiber significantly outperformed all other fibers.

Layers of CF panels, both virgin and recycled, were impregnated using a heated VARTM process with EPON 862 and W catalyst at a 100:26 mix ratio. The high temperature version of VARTM keeps the mold and resin at an elevated temperature during processing. The flow rate of resin through the test panels was 0.25 in/min, and the process used double-bagging for consistent thickness. Before the infusion process began, the resin and curing agent were mixed for five minutes, then heated and degassed for 20 minutes. After the resin was infused through the carbon fiber layers, post curing was performed at 121°C for four hours using one hour ramp up and down times in an autoclave.

VARTM Set #1

The first set of R-CFRP panels fabricated using VARTM used the four RCF sets derived from A-03 CFRP (Table 2). The reclaimed fiber mats were cut into 6" x 6" squares then impregnated with EPON 862 resin. Recycled fiber samples looked similar to the fiber shown in Figure 58 and were layered to attain a proper thickness.

Figure 58 – Representative reclaimed fiber sample exposed to the reclamation treatments used for the VARTM fabrication technique

Figure 59a shows the four VARTM panels fabricated with recycled carbon fiber. After formation of the R-CFRPs, specimens were prepared for mechanical testing by waterjet cutting (Figure 59b).

Figure 59 – (a) R-CFRP panels fabricated via the VARTM process, (b) waterjet cut test specimens

VARTM Set #2

The second experimental set used the treatments shown in Table 8 to recycle previously fabricated VARTM IM7 virgin panels. The IM7 carbon fiber was recovered and used to fabricate new R-CFRP panels using VARTM. The virgin CFRP originally contained EPON 862 resin. The R-CFRP samples were given the nomenclature MPC-2 and MPC-2+5. The 5 minute post treatment exposed the fibers to 1000°C in air.

Table 8 – Recycled VARTM composite panel treatment procedures

Sample	Reclamation Treatment	Air Post Treat
MPC-2	2 min	--
MPC-2 + 5	2 min	5 min

7.2 Mechanical Testing of VARTM Fabricated Panels

. Table 9 summarizes the ASTM standards followed for the mechanical testing of both VARTM and compression molded test panels. Although all five mechanical tests were not performed on one set of samples, some combination of test methods was.

Table 9 – Mechanical property testing matrix used to test virgin and recycled CFRPs

Mechanical Property	ASTM Standard Test #	ASTM Testing Name	Displacement Rate (in/min)
Tensile Strength	D3039	Tensile Properties of Polymer Matrix Composite Materials	0.05
Compression Strength	D3410	Compressive Properties of Polymer Matrix Composite Materials (Proc. B)	0.05
Interlaminar Shear Strength	D2344	Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates	0.02
Flexural Strength	D790	Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials	0.01

VARTM Set #1

The three different mechanical tests performed on the first set of re-fabricated composite panels included tension, compression, and interlaminar shear strength. Although the fabrication technique aimed to keep thickness differences of the panels to a minimum (denoted "h" in the following tables) between the recycled carbon fiber samples and the control sample, thickness differences existed in the VARTM set #1 panels. Thus, the results were most likely skewed due to this difference. In the following tables "b" represents the specimen width.

The composite panels were waterjet cut into approximately 4.25 x 0.75 inch specimens for tensile testing. The tensile test results are shown in Table 10. P^{max} represents the maximum load carried by the test coupon before failure, and F^{tu} represents the ultimate tensile strength in the testing direction.

Table 10 – Tensile testing results of CF reinforced EPON 862 fabricated using VARTM

Sample	Avg. b [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{tu} [MPa]	Avg. E [GPa]
Control IM7 CFRP	1.87 (0.02)	0.33 (0.00)	33,511 (3,493)	547 (57)	56.74
M4 R-CFRP	1.91 (0.00)	0.47 (0.02)	10,509 (3,141)	117 (38)	40.82
M4+5 R-CFRP	1.92 (0.02)	0.42 (0.01)	14,668 (2,972)	181 (38)	44.95
A2 R-CFRP	1.93 (0.01)	0.49 (0.01)	6,960 (569)	73 (6)	33.85
A2+5 R-CFRP	1.92 (0.04)	0.42 (0.02)	14,069 (359)	175 (13)	41.51

The thinnest samples performed the best in the tensile test apparatus. However, all of the R-CFRPs performed very poorly compared to the virgin fiber reinforced panels. The R-CFRP exhibiting the best ultimate tensile strength was M4+5. However, a 67% reduction in tensile strength is not very promising. The A2 R-CFRP was much worse only retaining 13% of the strength.

The next mechanical test performed on the five CFRPs was compression testing. P^{max} represents the maximum force obtained before failure. F^{cu} is the ultimate compressive stress, or compressive strength. The modulus of elasticity in the test direction is E. Table 11 reveals that the R-CFRPs retained 50%-87% of the compressive strength. M4+5 R-CFRP produced the best compressive strength of the reclaimed fiber composite samples (87% compressive strength retention), which is quite promising. The elastic modulus of A2 R-CFRP was the highest of the four experimental samples, and quite comparable to the control IM7 CFRP. Figure 60 reveals the ultimate tensile strength and compressive strength of the first set of VARTM fabricated CFRPs.

Table 11 – Compression testing results of CF reinforced EPON 862 fabricated using VARTM

Sample	Avg. b [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{cu} [MPa]	Avg. E [GPa]
Control IM7 CFRP	1.92 (0.01)	0.33 (0.00)	28,736 (296)	459 (1)	60.67
M4 R-CFRP	1.91 (0.01)	0.45 (0.04)	24,646 (5,590)	291 (90)	49.09
M4+5 R-CFRP	1.89 (0.01)	0.42 (0.01)	31,400 (5,232)	398 (76)	42.89
A2 R-CFRP	1.91 (0.03)	0.44 (0.01)	22,615 (2,705)	268 (31)	56.67
A2+5 R-CFRP	1.89 (0.02)	0.45 (0.02)	28,319 (2,716)	335 (43)	31.03

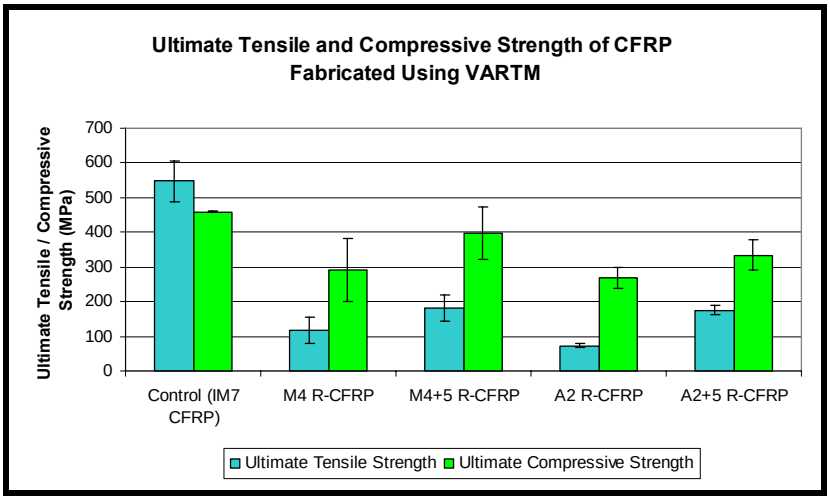

Figure 60 – Ultimate tensile and compressive strength of CFRP panels fabricated using VARTM

Table 12 reveals the data collected from the interlaminar shear strength testing. This test was performed as a modified 4-point method, rather than the 3-point method which the standard suggests. Shown in Table 12, b and h represent the specimen width and thickness respectively. P_{max} is the maximum load observed during the test. The short beam strength is represented by F^{sbs}.

Table 12 – Interlaminar shear strength testing results of CF reinforced EPON 862 fabricated using VARTM

Sample	Avg. b [cm]	Avg. h [cm]	Avg. P_{max} [N]	Avg. F^{sbs} [MPa]
Control IM7 CFRP	2.52 (0.01)	0.33 (0.00)	3,572 (75)	32.07 (0.64)
M4 R-CFRP	2.53 (0.01)	0.45 (0.01)	4,771 (228)	31.73 (2.13)
M4+5 R-CFRP	2.52 (0.00)	0.45 (0.00)	4,957 (474)	32.73 (2.99)
A2 R-CFRP	2.52 (0.01)	0.47 (0.00)	3,772 (96)	23.77 (0.55)
A2+5 R-CFRP	2.55 (0.01)	0.43 (0.01)	5,637 (676)	39.01 (4.84)

M4 and M4+5 R-CFRPs performed quite well compared to the IM7 control CFRP's interlaminar shear strength. Moreover, the M4+5 and A2+5 R-CFRPs actually outperformed the virgin carbon fiber reinforced control sample. Again, the discrepancy in thickness of the test panels possibly could have contributed to the enhancement of interlaminar shear strength. In addition, the A2 R-CFRP performed the worst of all the CFRP samples (only 74% strength retention).

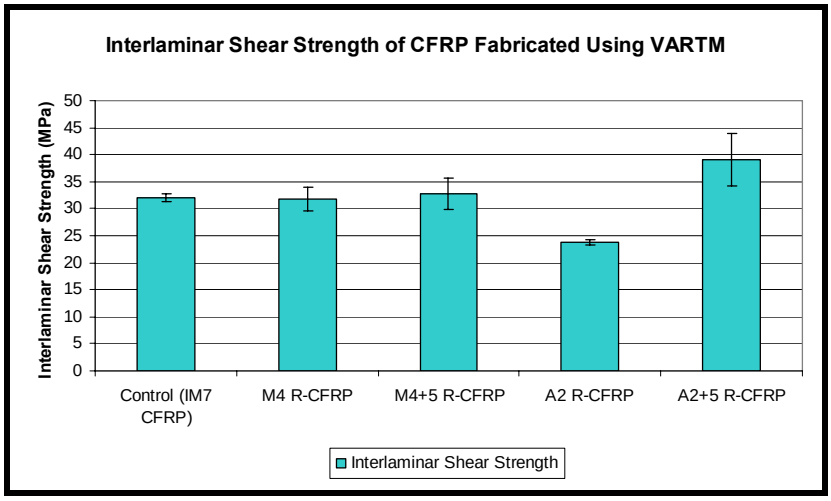

Figure 61 – Interlaminar shear strength of CFRP panels fabricated using VARTM

VARTM Set #2

The second series of reconstructed composite panels produced using VARTM was exposed to both tensile and compression testing. Table 13 and Table 14 reveal the tensile and compression properties of the CFRPs respectively. The CFRP thicknesses were very similar for this set, suggesting a more accurate comparison of tensile and compressive properties.

Table 13 – Tensile testing results of CF reinforced EPON 862 fabricated using VARTM

Sample	Avg. w [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{tu} [MPa]	Avg. E [GPa]
Control IM7 CFRP	1.87 (0.01)	0.33 (0.00)	33,511 (3,025)	547 (49)	56.74
MPC-2 R-CFRP	1.92 (0.00)	0.30 (0.01)	12,453 (1,191)	216 (23)	51.71 (4.48)
MPC-2+5 R-CFRP	1.92 (0.01)	0.32 (0.03)	14,605 (2,177)	239 (15)	56.81 (8.69)

Table 14 – Compression testing results of CF reinforced EPON 862 fabricated using VARTM

Sample	Avg. w [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{cu} [MPa]	Avg. E^{c} [GPa]
Control IM7 CFRP	1.92 (0.01)	0.33 (0.00)	28,736 (296)	459 (1)	60.67
MPC-2 R-CFRP	1.88 (0.08)	0.28 (0.02)	17,531 (4,673)	332 (74)	50.47 (0.90)
MPC-2+5 R-CFRP	1.92 (0.01)	0.29 (0.03)	18,774 (3,230)	340 (45)	40.75 (9.58)

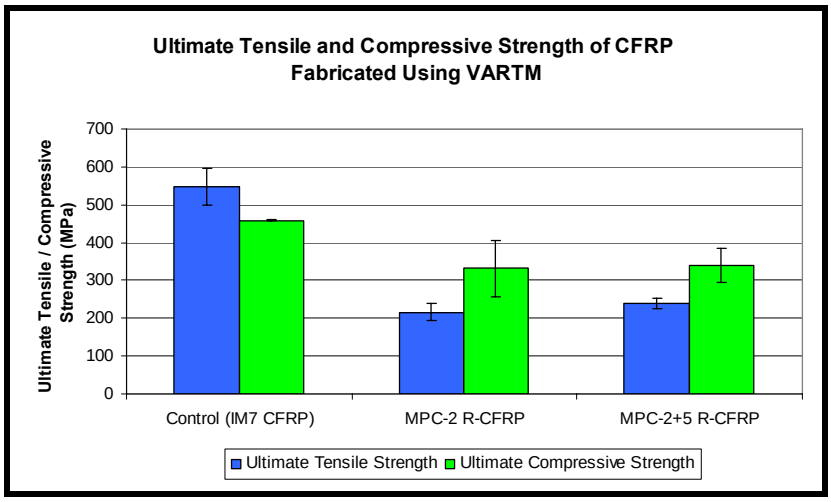

Figure 62 – Ultimate tensile and compressive strength of CFRP fabricated using the VARTM technique

As shown in Table 13, the tensile strength decreased significantly as a result of the reclamation and the thermal oxidative treatments. The R-CFRPs retained only 40% - 44% of the tensile strength. However, the modulus or stiffness of the composite test specimens was quite comparable to the virgin fiber control panel. Furthermore, the average compression strength of the recycled fiber panels was about 25% less than that of the control panel, as shown in Table 14.

The tension and compression test results indicate the reclamation and thermal post treatments have a fairly significant effect on diminishing the tensile strength and compressive strength of the carbon fibers when re-fabricated into new composites. However, these results are still promising due to the recycled fibers not having any sizing. The R-CFRPs still maintained approximately 50% of their strength. Also, the RCFs are most likely intermediate modulus fibers (AS4) and are being compared to a high modulus sized IM7 fiber.

7.3 Recycled Carbon Fibers Integrated via VARTM - Conclusions

Successful integration of recycled carbon fibers into polymer matrices via VARTM was achieved. Composite panels were actually fabricated utilizing recycled carbon fibers and then cut for mechanical testing. The resin did in fact bond with the fibers forming a R-CFRP. The mechanical properties were diminished in most all cases, and extremely low in others. The reclamation technique yielding the M4+5 RCFs performed the best when compared to the virgin IM7 fiber reinforced panels. This fiber and resin combination most likely had the best fiber to resin adhesion. However, this reclaimed fiber did not exhibit the best mechanical properties of the four reclaimed fibers with respect to SFTT. This places an emphasis on the surface properties of the fibers with respect to fiber to resin adhesion. The A2 R-CFRP performed the worst of the samples. This was mostly due to an inferior fiber modulus and poor fiber to resin adhesion.

The second set of reclaimed fibers also integrated well with the epoxy resin system. Composite panels were again fabricated successfully. It was expected that recycled IM7 fibers would have more strength than the RCFs in the first set, yielding enhanced mechanical properties. Even though the tensile strength of set #2 was significantly lower than the virgin IM7 reinforced composite, this set outperformed set #1. This is due to higher modulus fibers acting as the reinforcement material in the R-CFRP. The two recycled carbon fiber reinforced panels exhibited approximately a 55% reduction in tensile strength as well as a 25% reduction in compressive strength. The fibers most likely did not adhere to the resin as well as the control fiber. This can be attributed to the sizing present on the IM7 fiber. The sizing helped to promote adhesion between the fiber and resin.

7.4 Compression Molding Fabrication Technique

Compression molding was also used in the fabrication of R-CFRP panels. This procedure utilized chopped RCFs. Two different series of panels were fabricated using two slightly different sample preparation techniques before the actual compression molding. These two techniques were designed to simulate a BMC and a SMC for each respective set. It should be noted that a virgin fiber reinforced composite was not formulated for either series. The first set compared two reclaimed fibers with the same resin. The second set compared three different resin systems with the same recycled fiber.

Compression Molding Set #1

The first set of panels was produced using recycled carbon fibers labeled MC and MB2+5 using EPON 862 with W catalyst. Table 15 shows how the two recycled fiber samples were reclaimed.

Table 15 – Reclamation treatments for the two carbon fibers in the first series

Fiber Sample	Treatment	Recycled Fiber
MC	Continuous Pyrolysis Process	AS4
MB2+5	2 min Reclamation Treatment + 5 min Post Treat	Unknown

This particular composite preparation aimed to simulate a BMC. In order to determine the allowable amount of fibers by weight for the creation of 1/8" thick panels, the fibers were pressed in a 25 ton press while in a mold. Once the fibers in the mold measured approximately 1/8 inch in thickness, pressing was complete. The total amount of allowable carbon fibers was weighed, equaling approximately 60 g. EPON 862 and W catalyst were

then weighed and mixed equaling 200 grams, using a 100:26 mix ratio. The mixture was then poured onto the dry fibers and churned in a separate container until the fibers absorbed the resin completely. The materials were kneaded and rolled to ensure complete fiber wetting by the resin mixture.

The ball of material, essentially a BMC of carbon fibers and resin, was then placed in a Teflon® mold (Figure 63a) and pressed to all four corners. The top was placed on the mold, and 2000 lbs of pressure applied to the simulated BMC charge within the mold. The charge was then heated at 121°C and pressed for 5 hours to ensure the fibers were completely coated with resin. Figure 63 shows the compression molding sequence of a MB2+5 panel.

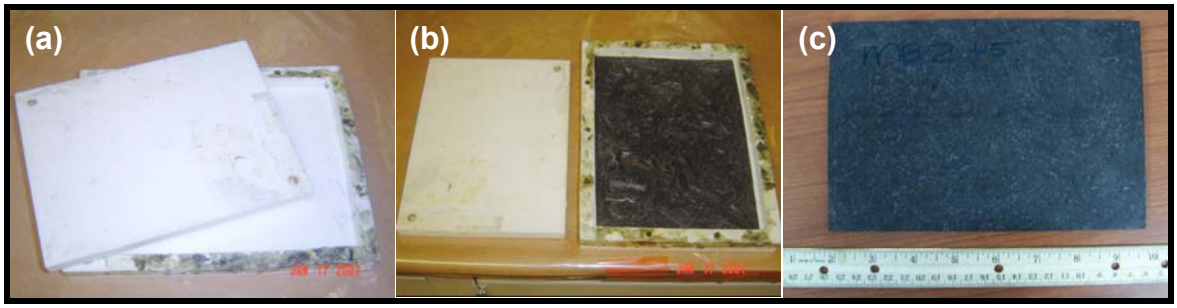

Figure 63 – Compression molding sequence of a panel (MB2+5)

After curing, the panels were cut to size and then weighed dry to determine mass, specific gravity, and density and allowing for the measurement of each panel's carbon fiber volume. The panel label scheme and measurements are shown in Table 16.

Table 16 – Recycled carbon fiber reinforced panel properties via compression molding

Panel	Dry Mass (g)	Wet Mass (g)	Volume (cc)	Density (g/cc)	Specific Gravity	Fiber Volume (%)
1MC R-CFRP	148.00	26.10	126.95	1.17	1.21	31.02
2MC R-CFRP	155.62	23.50	142.37	1.09	1.18	33.08
1MB2+5 R-CFRP	103.90	12.50	99.09	1.05	1.14	35.41
2MB2+5 R-CFRP	117.13	15.00	109.33	1.07	1.15	34.84

Compression Molding Set #2

A second series of panels was formulated using chopped recycled MC fibers (~1/2" in length). These fibers were mixed with three different resin systems: EPON 862, EPON 9504, and EPON 826. These panels were constructed simulating a SMC. The resin of choice was combined with the recycled MC fibers in a one gallon bag for mixing. The mixing process was then accelerated by pressing and kneading the plastic bag by hand. This was conducted until the fibers were well coated. The bag was then pressed using a rolling pin in order to remove voids and air pockets. The final rolled material was then placed into a Teflon® mold. The same curing parameters were used to create the SMC simulated compression molded panels as the BMC simulated compression molded panels.

The fiber volume percentages were obtained and are shown in Table 17 with the exception of the panel using EPON 826.

Table 17 – Recycled carbon fiber reinforced panel fiber volumes via compression molding

Resin Type	Average Panel Fiber Volume (%)
EPON 862	35
EPON 9504	34
EPON 826	Not Determined

7.5 Mechanical Testing of Compression Molding Fabricated Panels

Compression Molding Set #1

The first series of re-fabricated composite panels via compression molding were cut for tensile, compression, and flexure testing. It should again be noted that no control sample was fabricated and tested. A discrepancy in specimen thickness existed between the two sample sets.

Table 18 shows the tensile testing results for the compression molded test panels. The table indicates the MC R-CFRP had twice the tensile strength of MB2+5 R-CFRP. Figure 64 compares the two tensile strengths. However, the MB2+5 R-CFRP had a higher average tensile modulus. This type of data is valuable when tailoring recycled carbon fiber reinforced composites to particular applications, dependent on properties, such as stiffness.

Table 18 – Tensile testing results of R-CFRPs fabricated via compression molding

Sample	Avg. w [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{tu} [MPa]	Avg. E [GPa]
MC R-CFRP	1.40 (0.11)	0.47 (0.01)	2,291 (509)	34.56 (5.11)	13.31 (2.76)
MB2+5 R-CFRP	1.47 (0.04)	0.32 (0.04)	768 (220)	16.38 (3.37)	32.89 (21.99)

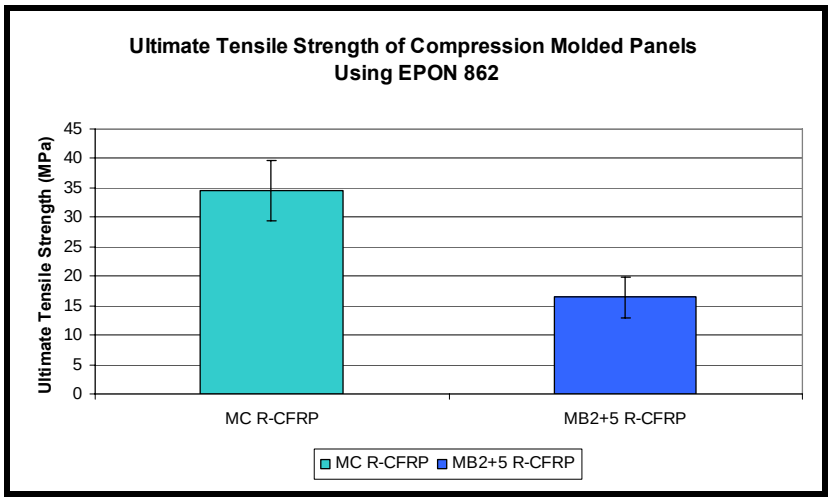

Figure 64 – Ultimate tensile strength of MC R-CFRP and MB2+5 R-CFRP fabricated via compression molding

Table 19 shows the flexure testing results from the composite panels reinforced with the two recycled carbon fibers. S_m and E_B represent the flexure strength as well as the flexural modulus respectively. Here, MB2+5 R-CFRP outperformed MC R-CFRP in both the average S_m as well as E_B. Figure 65 shows the comparison of the two flexural strengths.

Table 19 – Flexure testing results of R-CFRPs fabricated via compression molding

Sample	Avg. b [cm]	Avg. d [cm]	Avg. L [cm]	Avg. m [N/cm]	Avg. P_m [N]	Avg. S_m [MPa]	Avg. E_B [MPa]
MC R-CFRP	1.30 (0.10)	0.48 (0.02)	7.37 (0.00)	947 (98)	194 (10)	70.76 (4.80)	6,539 (1,293)
MB2+5 R-CFRP	1.20 (0.07)	0.34 (0.02)	5.59 (0.00)	795 (181)	145 (55)	88.40 (37.09)	7,506 (2,546)

Table 20 shows the compression testing results of MC R-CFRP and MB2+5 R-CFRP fabricated via compression molding. Figure 65 depicts the ultimate compressive strengths of the two samples. The results indicate that MC R-CFRP outperformed MB2+5 R-CFRP in compression strength. However, MB2+5 reinforced panels outperformed the MC R-CFRP with respect to the elastic modulus.

Table 20 – Compression testing results of R-CFRPs fabricated via compression molding

Sample	Avg. w [cm]	Avg. h [cm]	Avg. P^{max} [N]	Avg. F^{cu} [MPa]	Avg. E^{c} [GPa]
MC R-CFRP	1.49 (0.11)	0.48 (0.02)	8,197 (1,506)	113 (16)	11.51 (3.38)
MB2+5 R-CFRP	1.44 (0.03)	0.35 (0.02)	4,554 (1,167)	91 (22)	20.89 (3.93)

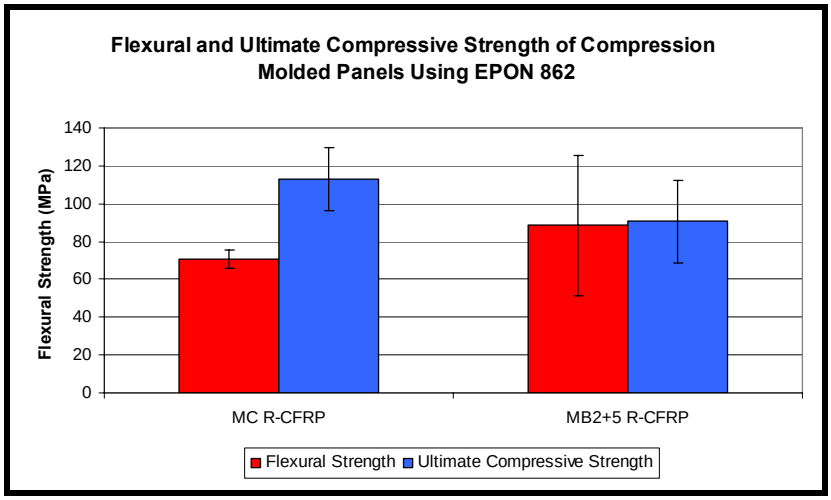

Figure 65 – Flexural and ultimate compressive strength of MC R-CFRP and MB2+5 R-CFRP fabricated via compression molding

The MB2+5 R-CFRP possessed the highest modulus for the three mechanical properties. However, it did not possess the highest tensile and compressive strength when compared to the MC reinforced specimens. Therefore if an application required a stiff material utilizing EPON 862, MB2+5 RCF would be the better reinforcing material of the two.

Compression Molding Set #2

The next series of panels fabricated via compression molding utilized MC recycled carbon fibers and EPON 862, 9504, and 826 resins. These panels were cut for tensile and

compression testing. Table 21 shows the tensile properties found. Figure 66 summarizes the ultimate tensile strengths of the three R-CFRPs. The results indicate that EPON 826 produces the composite panel with the best tensile strength and second best average modulus of the three. EPON 862 performed the worst of the three samples with respect to average tensile strength and average elastic modulus. This formulation did not possess even half the tensile strength of the EPON 826 and MC combination.

Table 21 – Tensile testing results of compression molded panels using three different resin systems

Sample	Avg. F^{tu} [MPa]	Avg. E [GPa]
EPON 862	16.06 (4.05)	7.03 (2.69)
EPON 9504	25.29 (2.79)	10.34 (2.34)
EPON 826	39.06 (4.98)	7.58 (1.86)

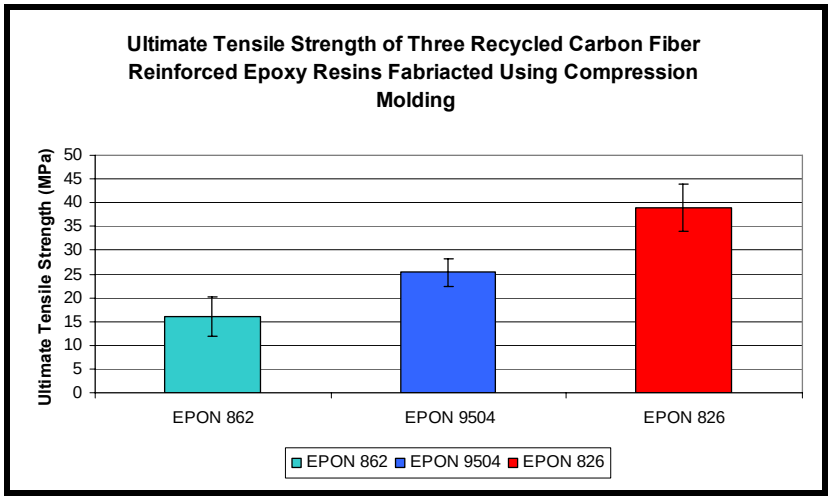

Figure 66 – Ultimate tensile strength of three recycled carbon fiber reinforced epoxy resins fabricated using compression molding

Table 22 shows the data obtained for the compression testing of the three different resin systems fabricated via compression molding. Figure 67 also illustrates their ultimate compressive strengths. The data shows the 862 resin system, coupled with the recycled

fibers, yielded the highest average compression strength as well as the highest average elastic modulus. This resin system performed the worst of the three resins with respect to the ultimate tensile strength. However, all three R-CFRPs had somewhat similar compressive strengths.

Table 22 – Compression testing results of compression molded panels using three different resin systems

Sample	Avg. F^{cu} [MPa]	Avg. E^{c} [GPa]
EPON 862	98.84 (16.10)	9.38 (2.14)
EPON 9504	82.20 (16.15)	9.17 (2.07)
EPON 826	96.16 (7.23)	5.58 (0.55)

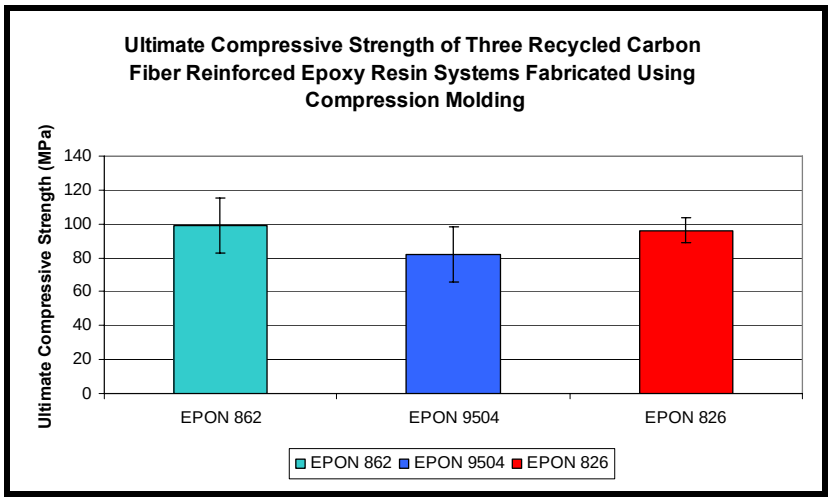

Figure 67 – Ultimate compressive strength of three recycled carbon fiber reinforced epoxy resins fabricated using compression molding

7.6 Recycled Carbon Fibers Integrated via Compression Molding - Conclusions

Compression molded panels were successfully fabricated using recycled carbon fibers. A control sample was not used in any of the compression molding trials. The first set of CFRPs compared two RCFs derived from two different fiber reclaimers using EPON 862 resin. The first set of compression molding trials showed that MC RCFs outperformed the

MB2+5 recycled fibers when embedded in EPON 862 with respect to the ultimate tensile strength and compressive strength. However, the MB2+5 fibers outperformed the MC fibers with respect to the flexural strength. This type of mechanical property difference is useful when selecting what type of fiber and resin system to use when designing applications to take advantage of specific material properties. If the component requires more flexural strength, then the MB2+5 reclaimed fibers would be most useful. However, if the component requires higher tensile and compressive strengths, the MC fiber would be the best candidate with EPON 862 epoxy resin.

The next set of compression molded panels also molded successfully utilizing reclaimed MC RCFs with three different epoxy resin systems. The EPON 826 resin clearly wetted the fibers better than the other two resins and outperformed them with respect to ultimate tensile strength. The EPON 826 and RCF combination also performed well with respect to compressive strength. However, the EPON 862 resin system coupled with RCFs slightly outperformed the EPON 826, yet there were no drastic differences among the three resin systems in this regard.

7.7 BMC Fabrication Technique

Compression molded plates were formulated using both virgin and recycled carbon fiber via a bulk molding compound. These plates were constructed by Bulk Molding Compounds, Inc. (BMCI) (Chicago, IL), the largest manufacturer of thermoset bulk molding compounds in North America. A total of 20 compression molded plates were manufactured. Ten plates labeled “VCF” incorporated virgin carbon fibers and ten plates labeled “RCF”

contained recycled carbon fibers. VCF was the control sample using milled PAN fibers. The PAN fibers were Asbury MF-0150 milled fibers with an average length of 150 μm. The milled recycled carbon fibers were provided by Milled Carbon Ltd., derived from their continuous pyrolysis process. The loading percentage was 2% by weight in each case. The plates were constructed using BMCI's compression molding grade vinyl ester bipolar plate compound labeled 8581.

The process of manufacturing BMC thermosets is geared toward high-volume, automated systems to ensure the highest quality at the lowest possible cost. BMC thermosets have also been designed to conduct electricity for use in applications such as bipolar plates used in fuel cells. The plates were molded at 160°C for 1 minute at a clamp tonnage of 45 tons for the 5" x 6" x 1/8" plaque. This equates to 3000 psi of pressure on the plaque surface. Figure 68 reveals the panels fabricated by BMCI.

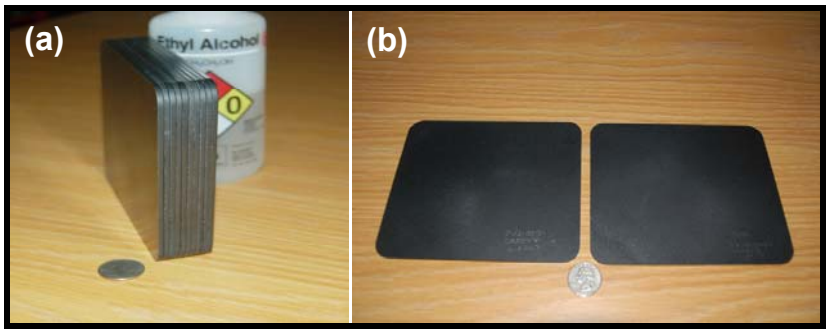

Figure 68 – BMC panels fabricated by BMCI using recycled carbon fibers and virgin carbon fibers

The test plaques were water jet cut by ADR Hydro-Cut (Morrisville, NC) into various test bars for both tensile and flexural mechanical testing. The standards were evaluated for the types of samples needed for the mechanical testing. A computer aided design (CAD) drawing was created for the testing and is shown in Figure 69.

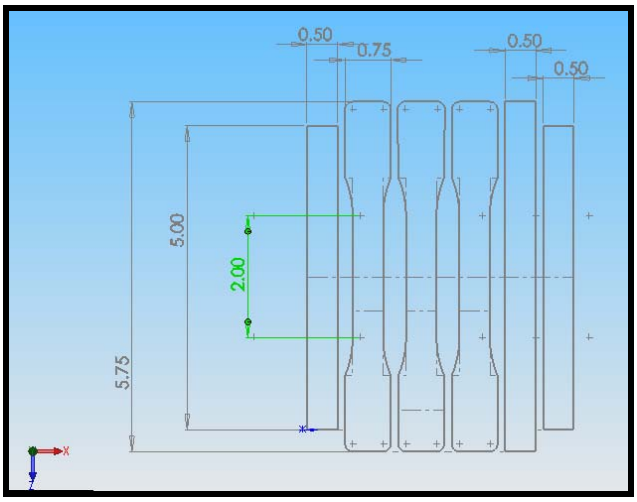

Figure 69 – CAD drawing used to waterjet cut test bars for mechanical testing

7.8 Mechanical Testing of BMC Fabricated Panels

Tensile testing was performed according to ASTM Standard D 3039. This test method determined the in-plane tensile properties of polymer matrix composite materials reinforced by carbon fibers. The crosshead speed used was 0.1 in/min. Flexural properties of the BMCI compression molded test panels were measured according to ASTM Standard D 790. These test methods cover the determination of flexural properties of unreinforced and reinforced plastics, including composite materials in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes. These test methods utilize a three-point loading system applied to a simply supported beam. The test bars were subjected to a constant extension rate of 0.06 in/min. The BMC plaque sequence is shown in Figure 70.

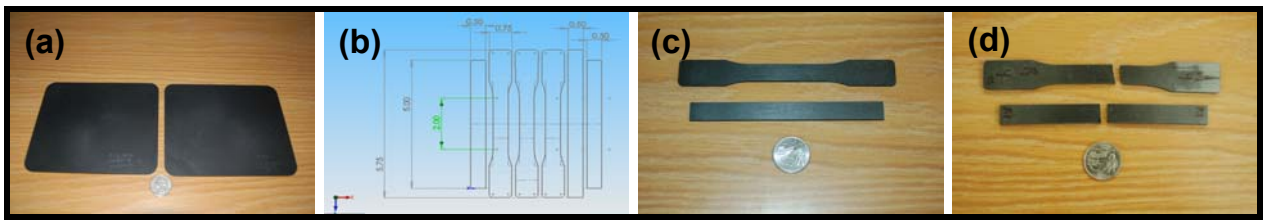

Figure 70 – (a) BMCI fabricated BMC panels, (b) CAD drawing, (c) waterjet cut test bars, (d) fractured test bars

The data for both the ultimate tensile strength and the flexural stress of both the virgin and recycled carbon fiber BMCI panels is illustrated in both Table 23 and Figure 71. The data reveals the virgin carbon fiber reinforced test bars have slightly higher ultimate tensile strength (UTS) and flexural stress averages in comparison to the RCF reinforced test bars. The average UTS and flexural stress values for the virgin carbon fiber reinforced test panels are 31.74 MPa and 47.46 MPa respectively. The average UTS and flexural stress for the recycled carbon fiber reinforced panels are 27.43 MPa and 47.09 MPa respectively. Thus, the virgin carbon fiber reinforced panels had a slightly better overall performance in both tensile and flexure modes. The recycled fiber reinforced panels had an 86.4% and 99.2% strength retention compared to the virgin fiber reinforced panels for the UTS and flexure stress respectively. These values are quite promising.

Table 23 – Ultimate tensile strength and flexure stress of virgin and recycled carbon fiber reinforced vinyl ester BMC panels fabricated by BMCI

Specimen # / Property	VCF Ultimate Tensile Strength [MPa]	RCF Ultimate Tensile Strength [MPa]	VCF Flexure Stress [MPa]	RCF Flexure Stress [MPa]
1	36.30	29.64	51.03	49.07
2	33.41	27.70	43.58	49.99
3	31.08	26.75	42.94	46.28
4	31.98	27.08	50.38	43.21
5	30.76	25.98	49.37	46.91
Average	**31.74 (2.47)**	**27.43 (1.38)**	**47.46 (3.89)**	**47.09 (2.65)**

Additionally, the recycled carbon fiber reinforced test bars had comparable average ultimate tensile strength and flexural stress values with commonly used commercial glass fiber reinforced plastic (GFRP) systems. A 22 wt. % glass reinforced polyester and Rostone's Rosite 5% glass reinforced polyester BMC have UTS values of 33.5 MPa and 20.7

MPa respectively. The 2% RCF BMC is clearly competitive with these commercial products (27.43 MPa). The 5% GFRP BMC also has a flexure strength of 52.0 MPa compared to the 47.1 MPa flexure strength of the 2% RCF BMC.

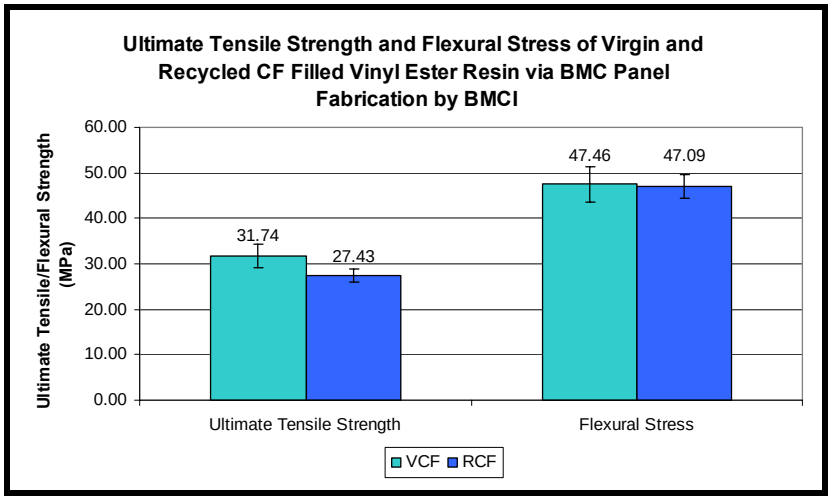

Figure 71 – Average tensile and flexure test data for virgin and recycled carbon fiber filled BMCI panels

7.9 Recycled Carbon Fibers Integrated via BMC - Conclusions

There was no considerable difference in mechanical properties between the R-CFRP panels and the virgin reinforced composite panels. This was expected due to the low loading percentages of carbon fiber (2% by weight). It was expected the virgin carbon fiber reinforced panel would slightly outperform the RCF panel, as it did with respect to both tensile and flexural strength. It was promising that the recycled carbon fibers, when mixed with the vinyl ester resin, exhibited similar properties to virgin fibers and other comparable materials. In fact the reclaimed carbon fibers behaved well in a BMC where the next step is formulating a BMC and fabricating a 3-D part.

7.10 Fabrication of a 3-D Compression Molded Part via a BMC

A three-dimensional compression molded part was fabricated using a phenolic resin-based BMC reinforced with recycled carbon fibers. A Rogers Hydraulic TCMSA-50-1716 compression molder with a 50 ton maximum load was used to fabricate a circuit breaker panel cover derived from a BMC charge reinforced with recycled carbon fibers. A mold was provided by Penn Compression Molding Inc. (Smithfield, NC).

The resin of choice was Plenco's 14399 phenolic due to the low smoke and toxicity levels emitted during burning. The 14399 resin is a resol that cross-links on its own without a catalyst and without an additional crosslinker. Generally, resols are cured by heating at elevated temperatures. The reinforcing fibers used were AS4 milled RCFs derived from Milled Carbon Ltd.'s continuous pyrolysis process. The other ingredients in the BMC formulation included mold release-Zinc Stearate, filler-Alumina Trihydrate SB-336, and catalyst-Trigonox 29B-75. The small amount of additional catalyst was added as a precautionary measure to insure fast curing during the compression molding process. The complete BMC formulation is seen in Table 24.

Table 24 – Recycled carbon fiber reinforced BMC compound used for compression molding

Component	Weight %
Resin - Plenco 14399 Phenolic	65.97
Filler - Alumina Trihydrate	21.40
Reinforcement - Recycled Carbon Fiber	11.60
Mold Release - Zinc Stearate	0.83
Catalyst - Trigonox 29B-75	0.20
TOTAL	**100.00**

The constituents of the BMC were mixed in a large beaker by hand ensuring the

carbon fibers and filler material were completely wetted by the phenolic resin. Two BMCs were formulated weighing 858 g and 918 g. The first BMC formulated was more viscous than the second one and was not used for the compression molding trials.

The BMCs were then refrigerated and transported to Penn Compression Molding Inc. The mold, as shown in Figure 72a, produces two circuit breaker panel covers. The original part uses a 30 g charge (on each side of the mold) and is compression molded at 160°C at 2,200 psi for 1.5 mins. Two 30 g recycled carbon fiber reinforced BMCs were compression molded at approximately 160°C (Figure 72b) at varying pressures and curing times. The two pressures, 500 and 2,200 psi, and three curing times, 1.5, 3, and 5 mins, were used to fabricate multiple parts keeping the mold temperature and charge weight constant. These variables were manipulated to obtain the best part fabrication parameters for the formulated BMC.

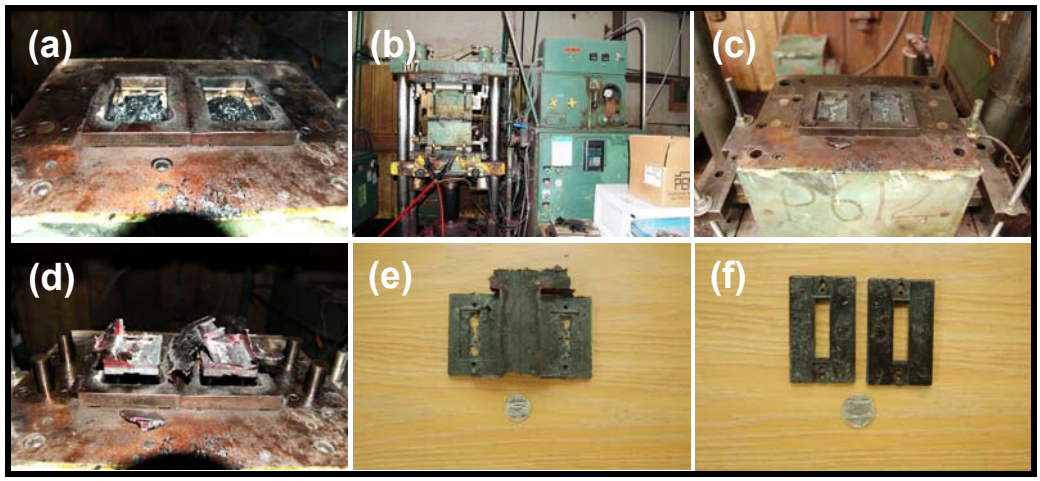

Figure 72 – Compression molding sequence fabricating a 3-D part comprised of recycled carbon fibers

Figure 72c and Figure 72d show the part when the pressure is released and when the part is ejected from the mold respectively. Remnant material left on the edges of the part, known as flash (Figure 72e), is then filed off producing a finished part (Figure 72f).

7.11 Fabrication of a 3-D Compression Molded Part via a BMC - Conclusions

Multiple 3-D parts were fabricated successfully at varying pressures and curing times. The temperature and weight of the charge were kept constant in each of the trials. The pressure and curing time was manipulated to determine which parameters produced the best looking part. The parts were not tested for their mechanical durability. The best looking part was fabricated at 500 psi and a curing time of 5 minutes. This part possessed the best surface finish, and the least amount of porosity. The best part fabricated using a pressure of 2200psi was cured for 3 minutes. Recycled carbon fibers showed the ability to be effectively formulated with a phenolic resin and other additives into a BMC, successfully fabricating a 3-D part.

8. Characterization of Boeing 787 Dreamliner RCF Material

8.1 Test Materials

Both recycled and virgin fibers were received from carbon fiber material suppliers for the Boeing 787 Dreamliner. Four fiber sets existed (CF1, CF2, CF3, and CF4). Virgin and recycled fibers contained nomenclature with a V and R, respectively, preceding the fiber set number (e.g., CF1 Set → VCF1 (virgin), RCF1 (recycled)). Samples of the recycled fibers were reclaimed by Milled Carbon Ltd. using their continuous pyrolysis process. In this

research, Milled Carbon Ltd. previously used EOL composite scrap as their feedstock. These four samples were derived from manufacturing scrap in Boeing's production facilities in Washington. Characterization techniques including SEM, XPS, and SFTT were used to analyze the fibers.

Figure 73 reveals the CF1 fiber set showing the different morphology of the fiber samples. RCF1 is uncured unidirectional fiber in a long continuous bundle. This represented the entire sample received by NC State. Furthermore, VCF1 represents the control fiber for both RCF1 and RCF3. VCF1 also contains sizing on the surface of the fibers.

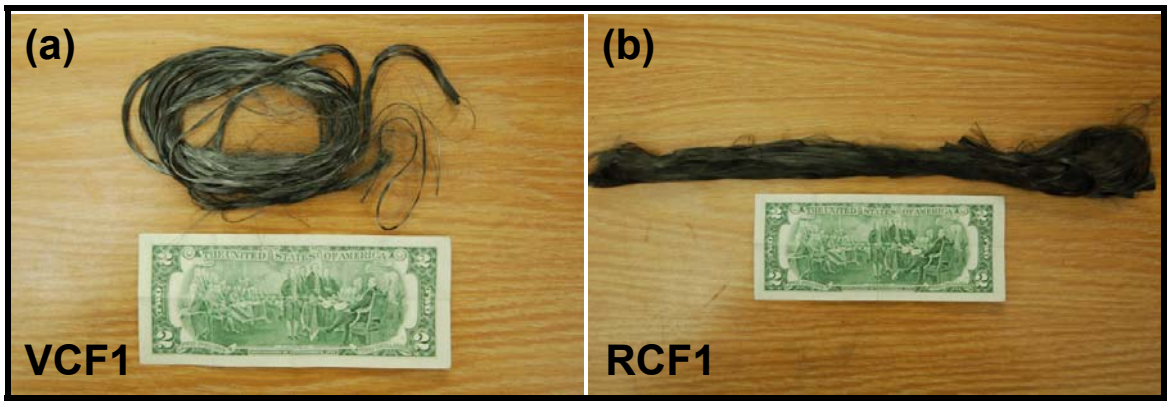

Figure 73 – Carbon fiber set #1 of Toray T800SC 24K tow fiber: (a) Virgin VCF1, (b) Recycled RCF1

RCF2, as shown in Figure 74b, reveals the carbon fiber in woven morphology. This fiber sample is an uncured wide-tow fabric. The width of RCF2's tow is clearly distinguished from the other fiber samples. VCF2 also has a larger tow width compared to the other virgin samples.

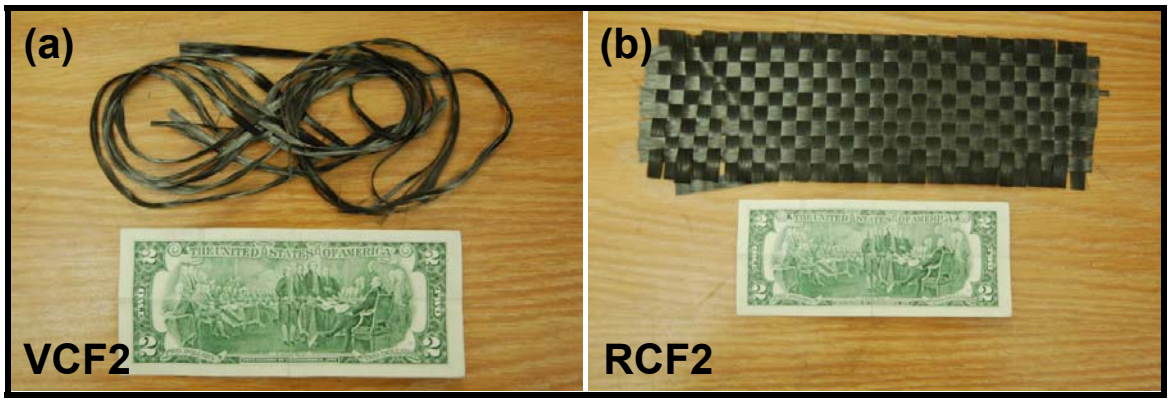

Figure 74 – Carbon fiber set #2 of Toray T700G 12K tow fiber: (a) Virgin VCF2, (b) Recycled RCF2

RCF3, shown in Figure 75b, has a morphology of chip-like pieces of carbon fiber. This sample contains pieces anywhere from 2 to 8 inches in length. The smaller pieces tend to be cut in a parallelogram shape. The longer pieces have a straight morphology in a rectangular form. These fibers seem to be the stiffest of all the carbon fibers when held. VCF1 corresponds to both RCF1 and RCF3. RCF3 is derived from cured part trimmings from the 787 Dreamliner.

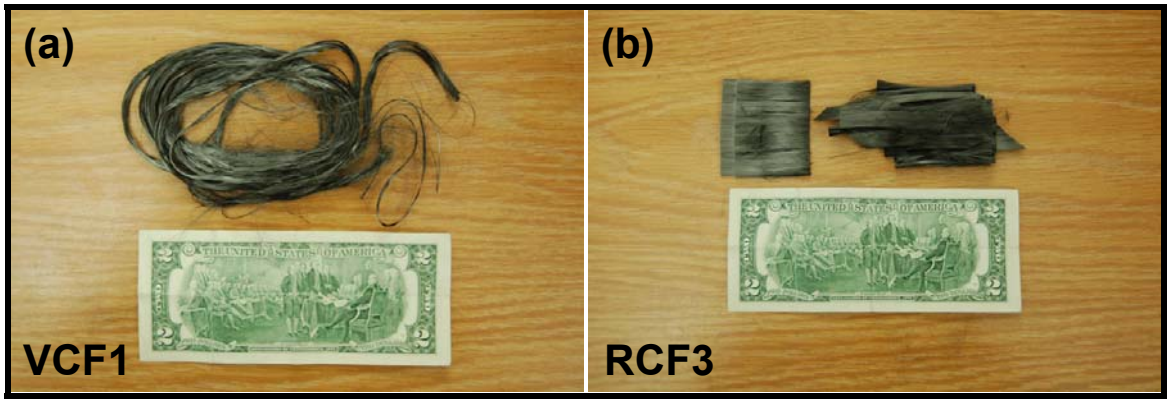

Figure 75 – Carbon fiber set #3 of Toray T800SC 24K tow fiber: (a) Virgin VCF1, (b) Recycled RCF3

RCF4, shown in Figure 76b, is a woven fabric in large pieces about 1 ft in length. This fiber set is derived from uncured fabric. Most likely this uncured fabric was

manufacturing scrap which came from a fiber lay-up. The image below shows a zigzag pattern on the fabric where a part was possibly cut out. The virgin fiber, shown in Figure 76a, is the tow used for the fabric weave.

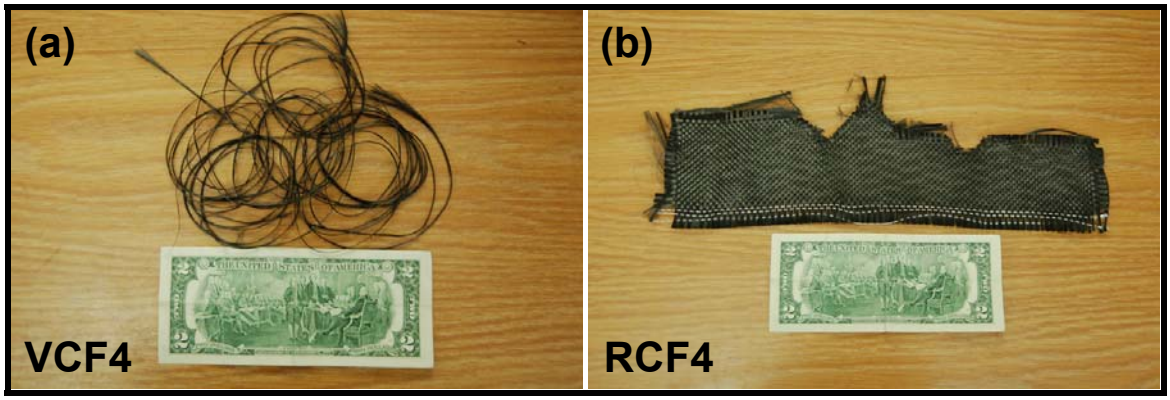

Figure 76 – Carbon fiber set #4 of Cytec T300H 3K tow fiber: (a) Virgin VCF4, (b) Recycled RCF4

The following information was obtained from the respective virgin fiber manufacturers. This information was found in the technical data sheets for each of the fibers.

The Toray T800SC 24K tow (VCF1) carbon fiber is an intermediate modulus, high tensile strength fiber, developed as a cost effective alternative to T800H. This never twisted fiber has excellent tensile composite properties and is specifically designed to meet the weight saving demand of aircraft and high performance recreational products.

Toray T700G 12K tow (VCF2) carbon fiber has an enhanced tensile modulus and adhesion properties over T700S. Applications of this never twisted fiber include aircraft and high performance sporting goods where demanding conditions require superior composite properties.

Cytec's T300 3K tow (VCF4) carbon fiber is an aircraft and aerospace grade carbon fiber with moduli slightly lower than those of the two other Toray fibers.

Table 25 – Manufacturer's data of material properties for the three control samples used in the research

Material Property	VCF1 (Toray T800SC 24K)	VCF2 (Toray T700G 12K)	VCF4 (Cytec T300 3K)
Tensile Strength (GPa)	5.88	4.90	3.75
Tensile Modulus (GPa)	294	240	231
Strain (%)	2.0	2.0	1.4
Filament Diameter (μm)	5	7	7
Sizing Type, Amount	10E, 0.5%	31E, 0.5%	Not Specified

8.2 Scanning Electron Microscopy

A Hitachi S-3200 variable pressure SEM was used to capture low magnification images from 1,000 to 2,500X. An accelerating voltage of 20 kV was used when examining the fibers. To gain a more detailed image of the fibers, a JEOL 6400F field emission SEM was used to obtain high magnification/resolution images for the fiber samples. Again, an accelerating voltage of 20 kV was used to examine the fibers. The magnifications obtained ranged from 5,000 to 20,000X.

The samples for both high and low magnification SEMs were cut to approximately 5-10 mm^2. The samples were mounted to an aluminum stub using double-sided carbon tape. All SEM analysis was conducted at AIF. Again, it should be duly noted that these images are representative of the entire fiber sample set.

Sample Set: CF1

Shown in Figure 77 at 1,000X magnification, the recycled fibers are quite comparable to the virgin fibers. No drastic differences exist between the morphologies of the two fiber

sets. However, some surface blemishes on RCF1's central fiber (Figure 77b) are present. Again, the recycled fibers are derived from uncured unidirectional fiber.

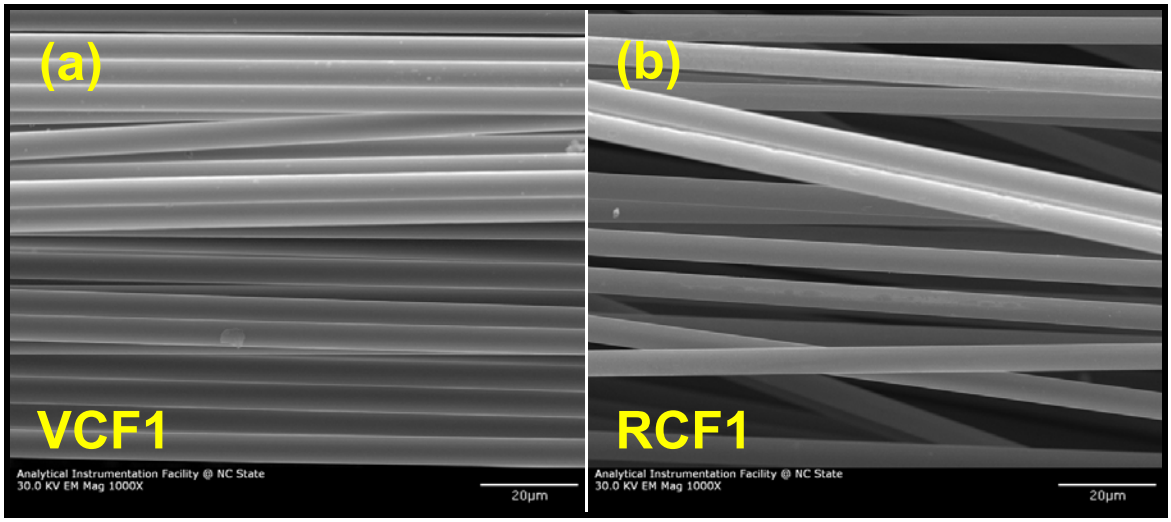

Figure 77 – Variable pressure SEM micrographs at 1,000X magnification for fiber sets (a) VCF1 and (b) RCF1

Figure 78 reveals the difference between the two fiber sets at 2,500X magnification. Figure 78b shows RCF1 has pitting on the surface of the fibers. However, this type of behavior was not found on the other images at higher magnifications. This pitting is most likely a result of the reclamation technique.

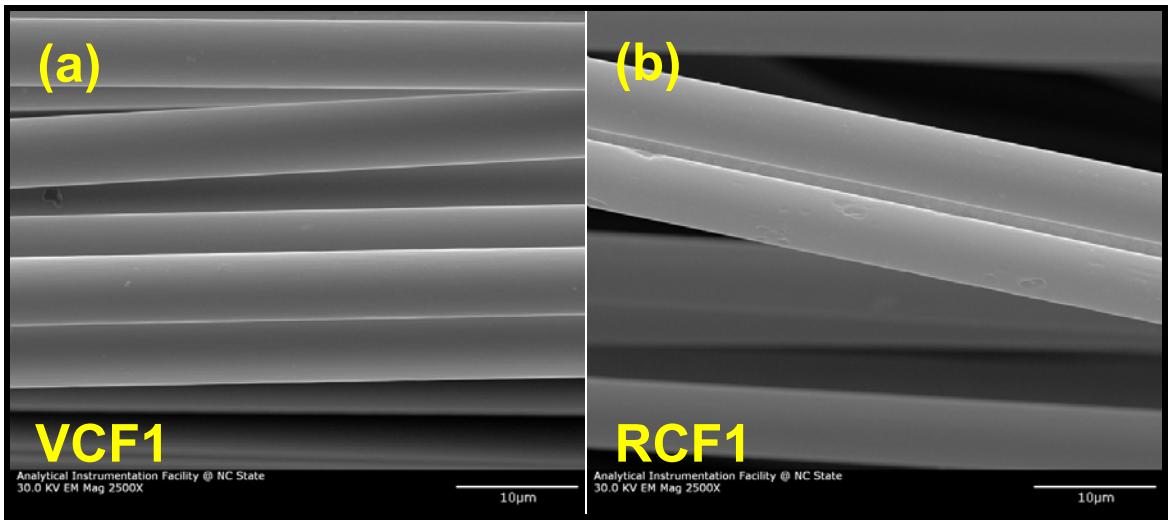

Figure 78 – Variable pressure SEM micrographs at 2,500X magnification for fiber sets (a) VCF1 and (b) RCF1

The field emission scanning electron microscope was used to obtain images at magnifications of 5,000X, 10,000X and 20,000X. The cleanliness of the fibers, both virgin and recycled, is clearly seen in Figure 79 at 5,000X magnification. The RCFs derived from manufacturing scrap are much cleaner than RCFs derived from EOL scrap previously analyzed.

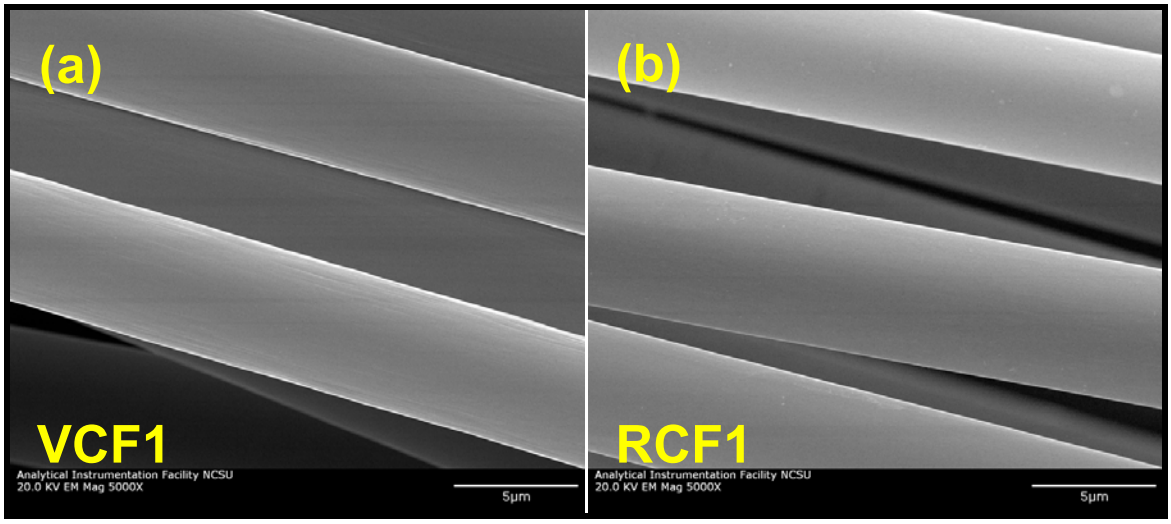

Figure 79 – Field emission SEM micrographs at 5,000X magnification for fiber sets (a) VCF1 and (b) RCF1

The field emission SEM does a better job revealing the striations present on the surface of the fibers than the variable pressure SEM. Figure 80 reveals RCF1 does not have striations dominantly present on the surface of the fibers. The reclamation treatment could have influenced this.

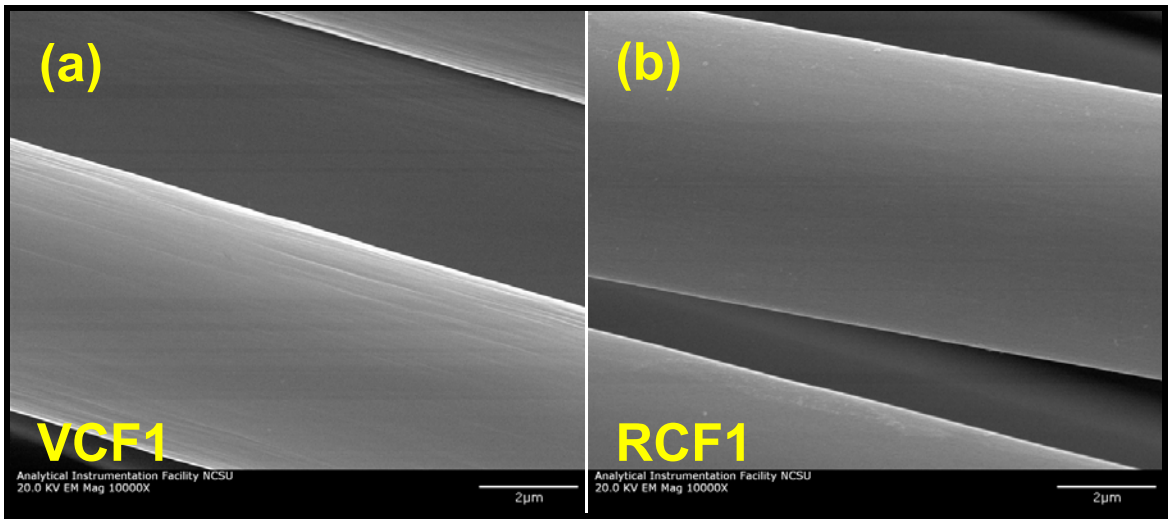

Figure 80 – Field emission SEM micrographs at 10,000X magnification for fiber sets (a) VCF1 and (b) RCF1

Again, striations are present on the surface of VCF1 in Figure 81a at 20,000X magnification. There also seems to be some sort of residue present on the surface of RCF1 at this magnification in Figure 81b.

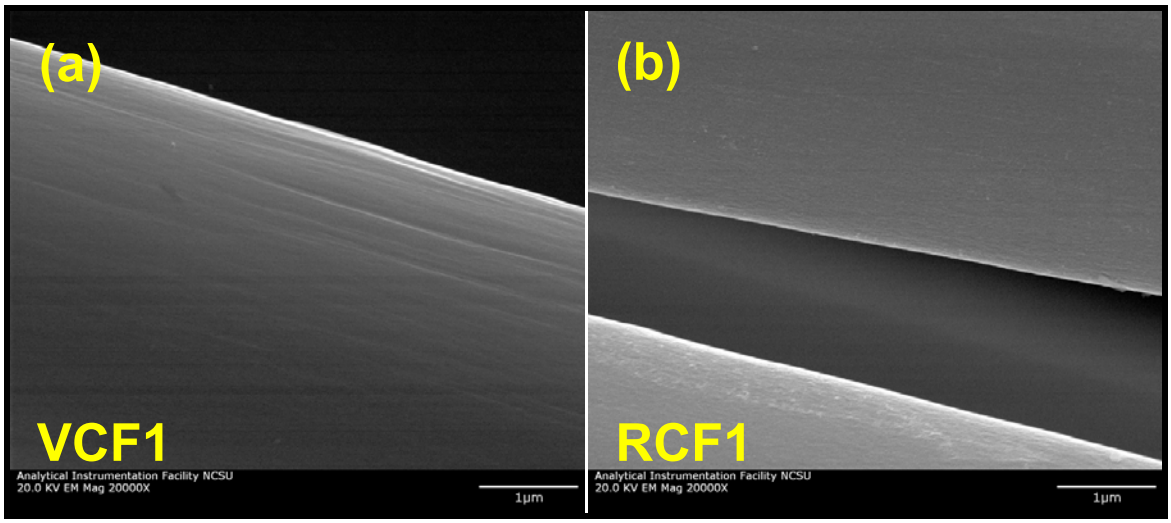

Figure 81 – Field emission SEM micrographs at 20,000X magnification for fiber sets (a) VCF1 and (b) RCF1

Sample Set: CF2

RCF2 is derived from an uncured wide tow fabric. The two fiber samples, shown below in Figure 82, have similar morphologies, and are quite comparable at 1,000X magnification. Surface blemishes are present on RCF2's lower fibers in Figure 82b. These surface blemishes are much more defined using the field emission SEM.

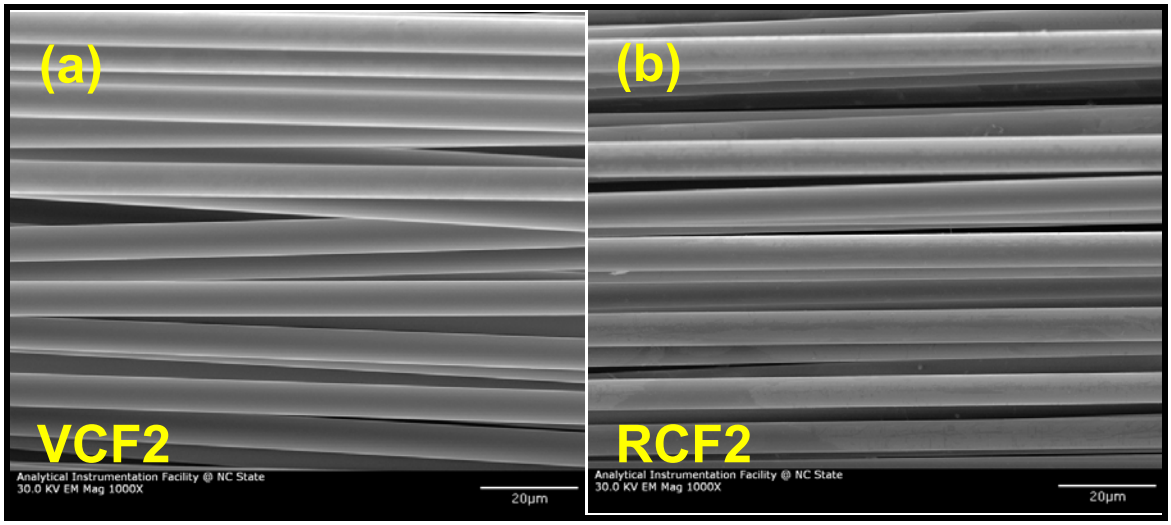

Figure 82 – Variable pressure SEM micrographs at 1,000X magnification for fiber sets (a) VCF2 and (b) RCF2

Figure 83 shows the similarity between the virgin and recycled fiber sets at 2,500X magnification. Both sets of fibers are very clean. Again, slight surface blemishes are present on the recycled fibers in Figure 83b.

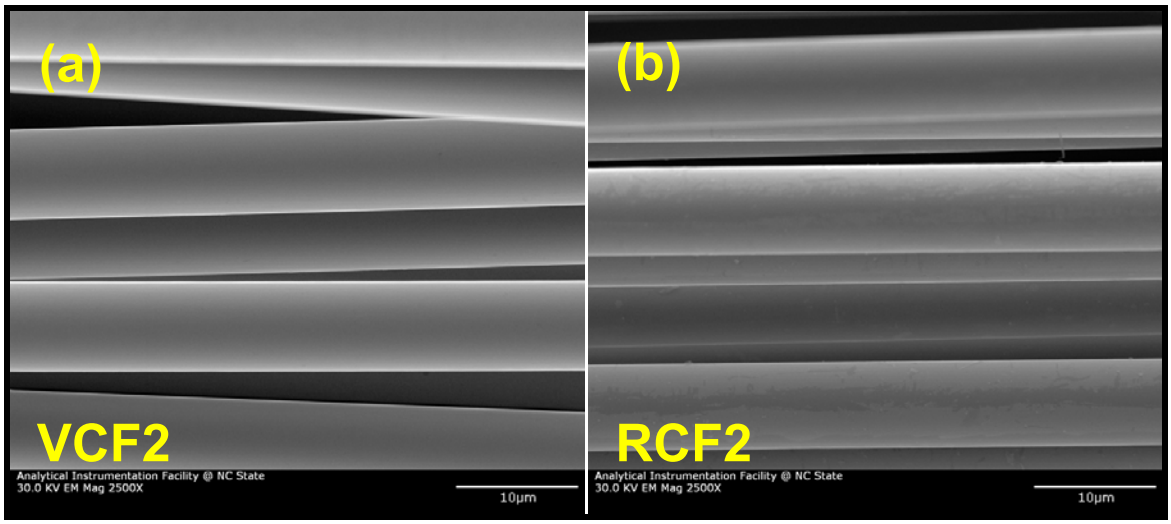

Figure 83 – Variable pressure SEM micrographs at 2,500X magnification for fiber sets (a) VCF2 and (b) RCF2

RCF2's surface blemishes are more defined using the field emission SEM in Figure 84b. There also are some particulates present on the surface of these fibers. Furthermore, small markings were present on VCF2's surface. These markings were seen throughout all images and areas on the sample.

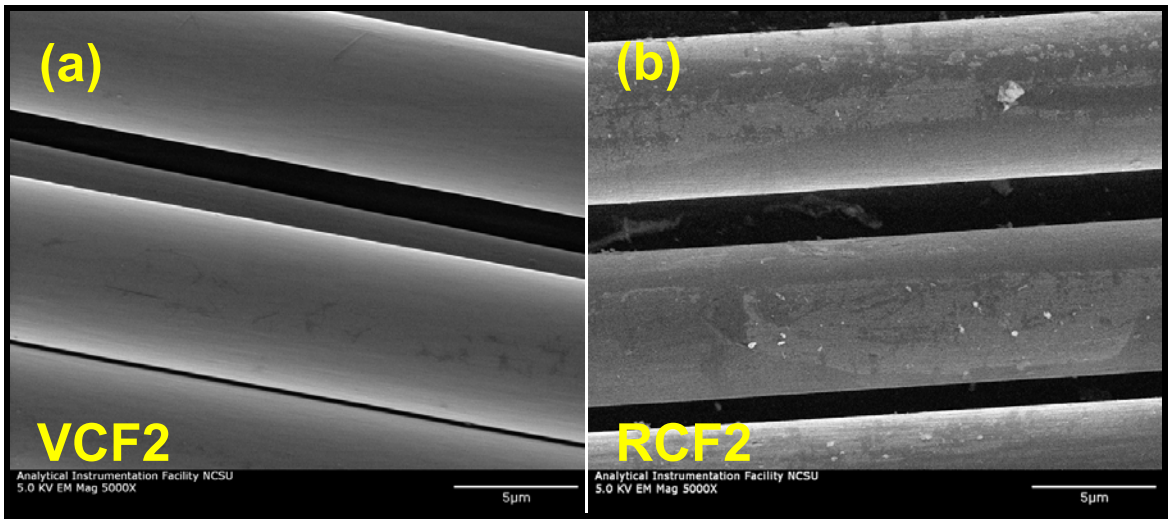

Figure 84 – Field emission SEM micrographs at 5,000X magnification for fiber sets (a) VCF2 and (b) RCF2

The two fiber sets are shown in Figure 85 at 10,000X magnification. The recycled fiber still contains particulates present on the surface of the fibers. Also, the striations are more prevalent for RCF2 than VCF2. This type of surface behavior is seen in more detail in Figure 86.

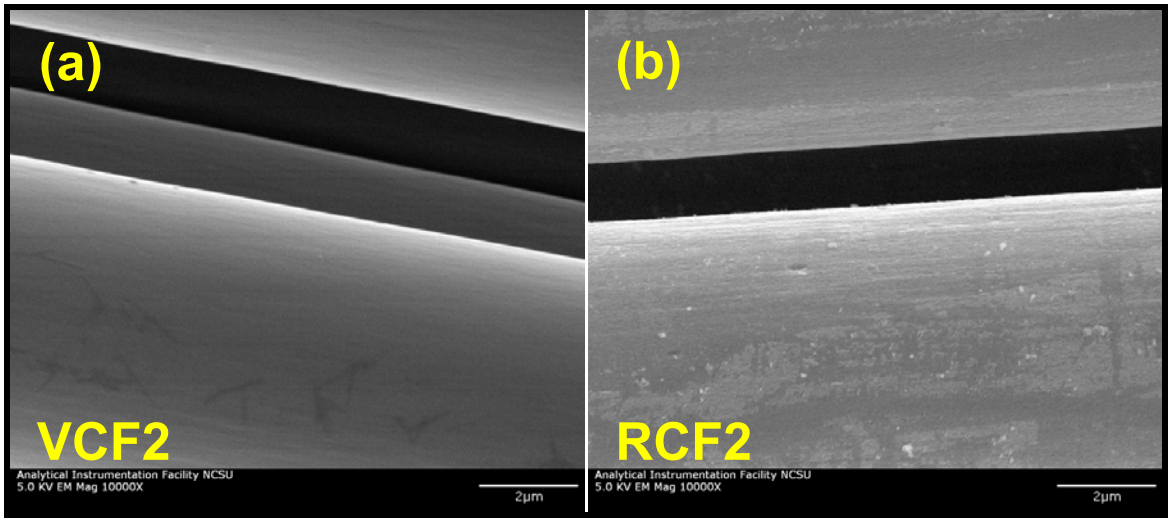

Figure 85 – Field emission SEM micrographs at 10,000X magnification for fiber sets (a) VCF2 and (b) RCF2

The striations on the surface are clearly seen for both fiber sets at 20,000X magnification in Figure 86. RCF2 has deeper striations compared to VCF2. It is also evident that VCF2 is cleaner than RCF2. In this case the reclamation technique might not influence the striations on the fiber surface.

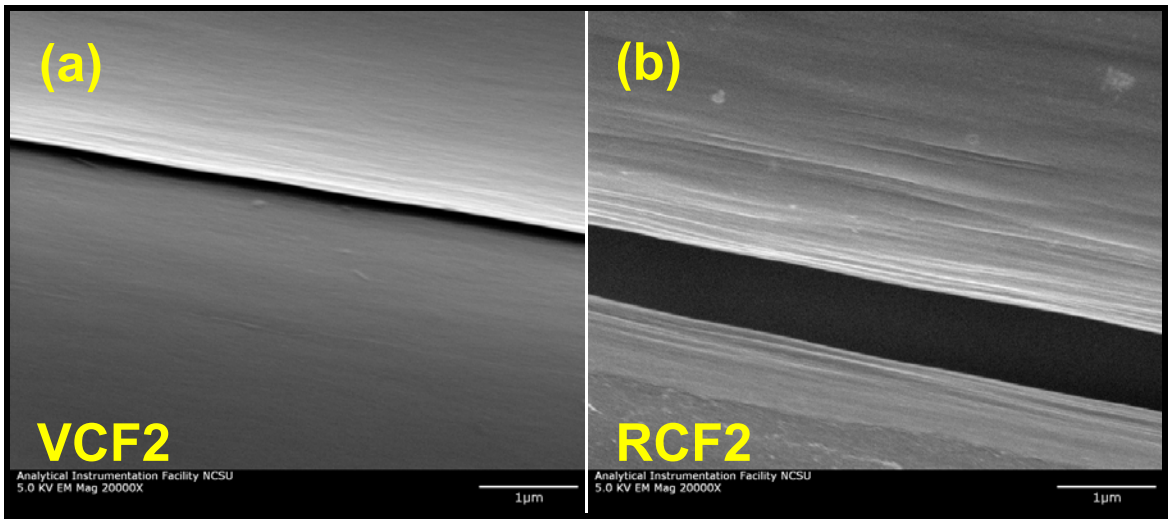

Figure 86 – Field emission SEM micrographs at 20,000X magnification for fiber sets (a) VCF2 and (b) RCF2

Sample Set: CF3

The recycled fiber set RCF3 was derived from cured composite 787 Dreamliner part trimmings. Figure 87 reveals the fibers at 1,000X magnification. Some type of residue is present in the middle to lower half of Figure 87b for RCF3. Some fibers are crossing due to the sample preparation. RCF3 had a somewhat loose arrangement.

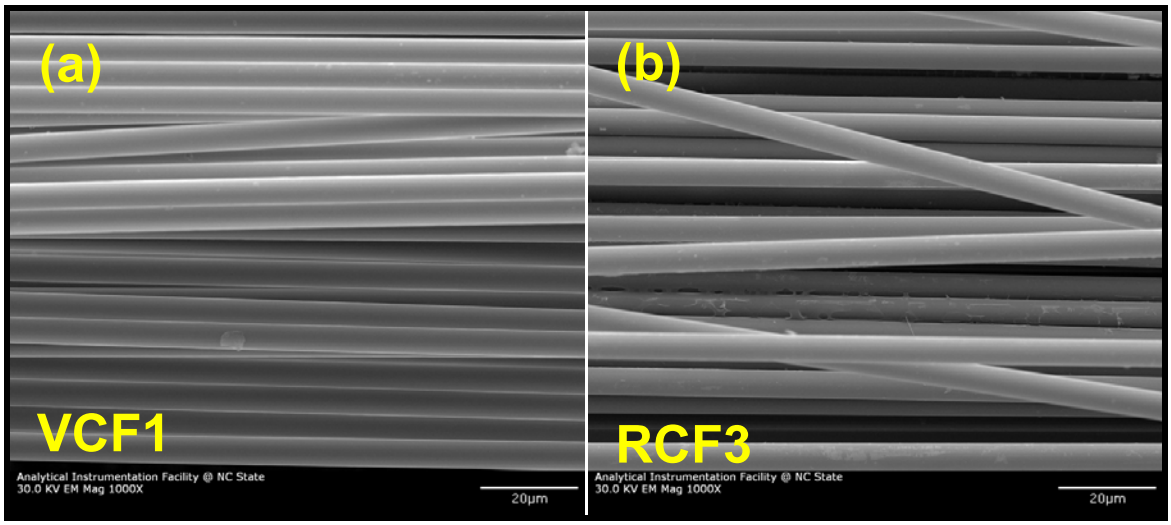

Figure 87 – Variable pressure SEM micrographs at 1,000X magnification for fiber sets (a) VCF1 and (b) RCF3

The residue is clearly seen in Figure 88b for the recycled fiber. Some resin or residue still exists on the surface of the fibers that the reclamation technique did not remove. Simply handling RCF3, there is a degree of stiffness which would indicate resin is still present on the fibers. The other 3 samples involved in the Boeing 787 material research are derived from carbon fiber which was uncured and did not exhibit this stiffness.

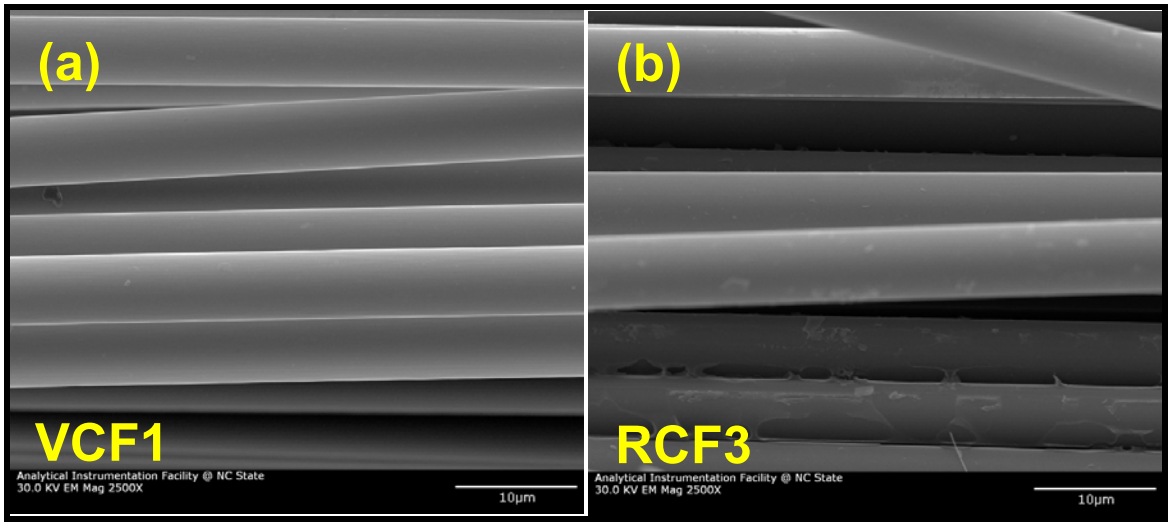

Figure 88 – Variable pressure SEM micrographs at 2,500X magnification for fiber sets (a) VCF1 and (b) RCF3

Slight striations are still present on the surface of RCF3 at 5,000X magnification. Also, particulates are on the surface of RCF3, in Figure 89b.

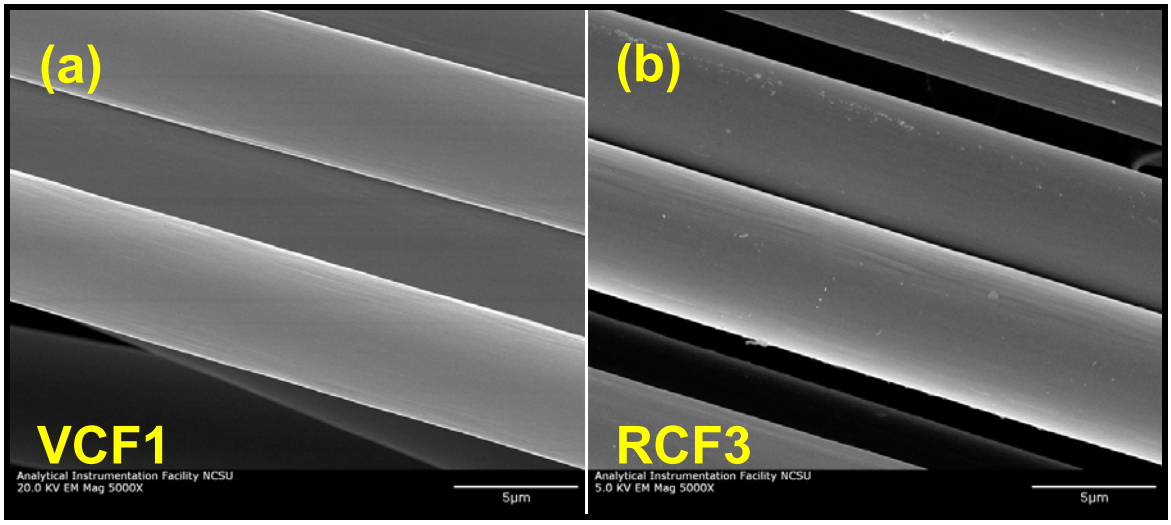

Figure 89 – Field emission SEM micrographs at 5,000X magnification for fiber sets (a) VCF1 and (b) RCF3

RCF3, shown in Figure 90b, seems very smooth, yet there is no strong presence of residue on the fiber. RCF3 is very similar to VCF1 in these images. This indicates that even RCFs derived from cured manufacturing scrap are quite comparable to virgin material.

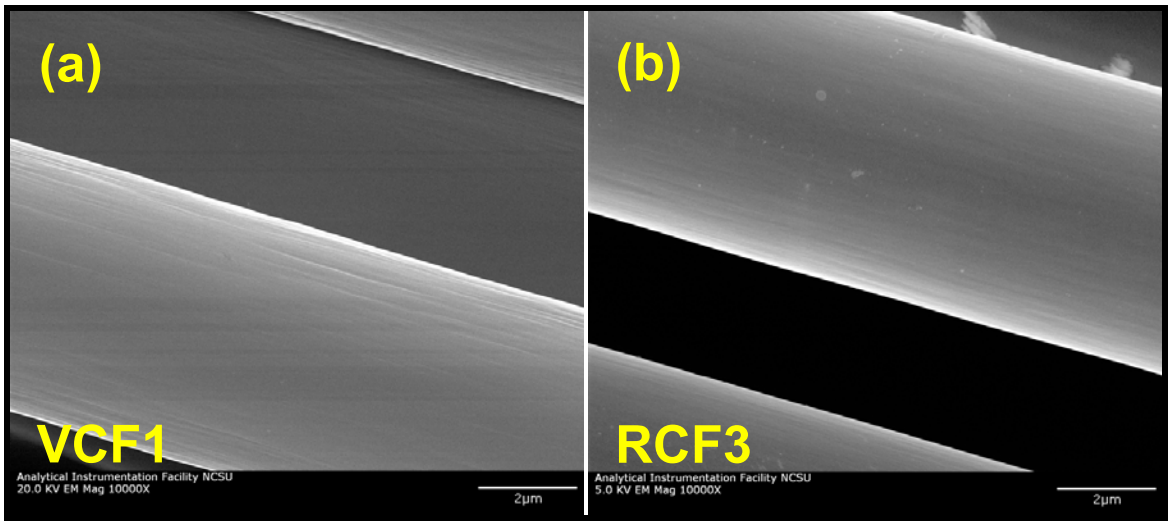

Figure 90 – Field emission SEM micrographs at 10,000X magnification for fiber sets (a) VCF1 and (b) RCF3

At 20,000X magnification the fiber surfaces seem very similar and have comparable surface morphology. This behavior is evident in Figure 91. Small particulates do exist on RCF3 however.

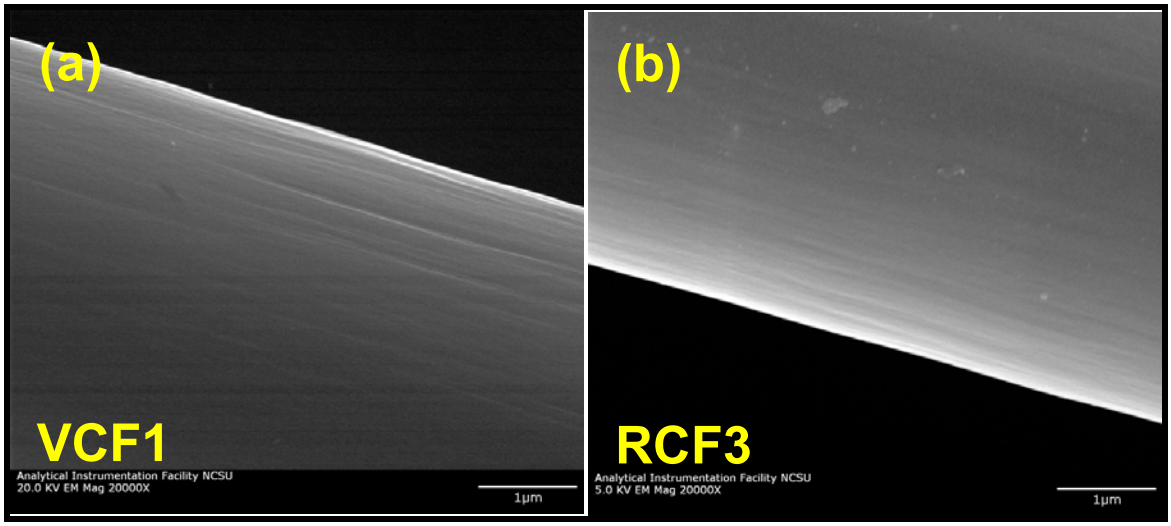

Figure 91 – Field emission SEM micrographs at 20,000X magnification for fiber sets (a) VCF1 and (b) RCF3

Sample Set: CF4

The final sample set observed under the SEM was CF4. The recycled fiber contained in this sample set (RCF4) was derived from an uncured fabric. Figure 92 shows the two fiber sets at 1,000X magnification. Some forms of particulates are present on both the fiber sets, but more so on VCF4.

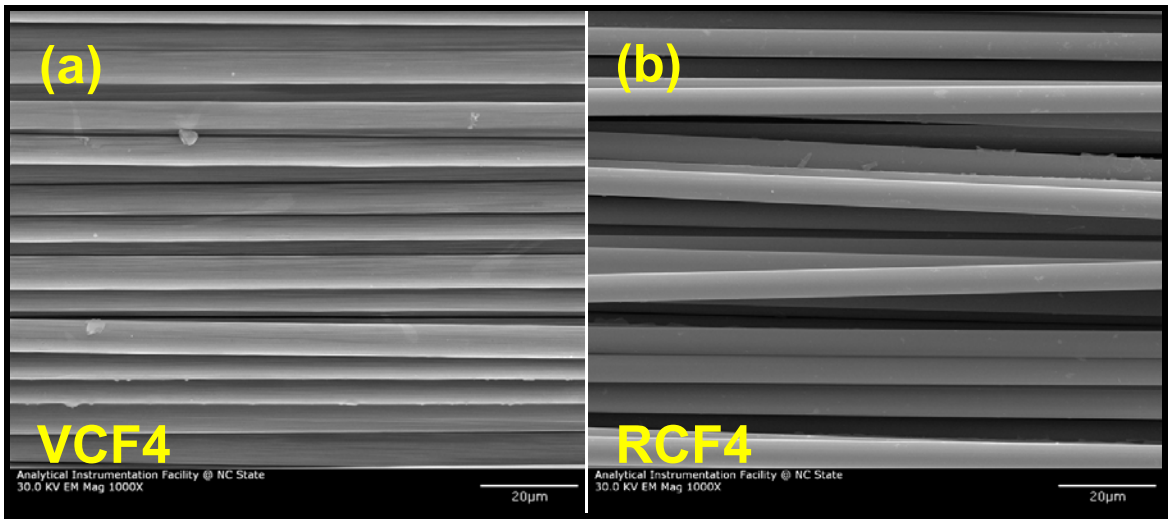

Figure 92 – Variable pressure SEM micrographs at 1,000X magnification for fiber sets (a) VCF4 and (b) RCF4

The variable pressure SEM even reveals the strong presence of striations for the virgin sample (VCF4) in Figure 93a at 2,500X magnification. Some surface blemishes and particulates are also present on the lower part of the micrograph in Figure 93b.

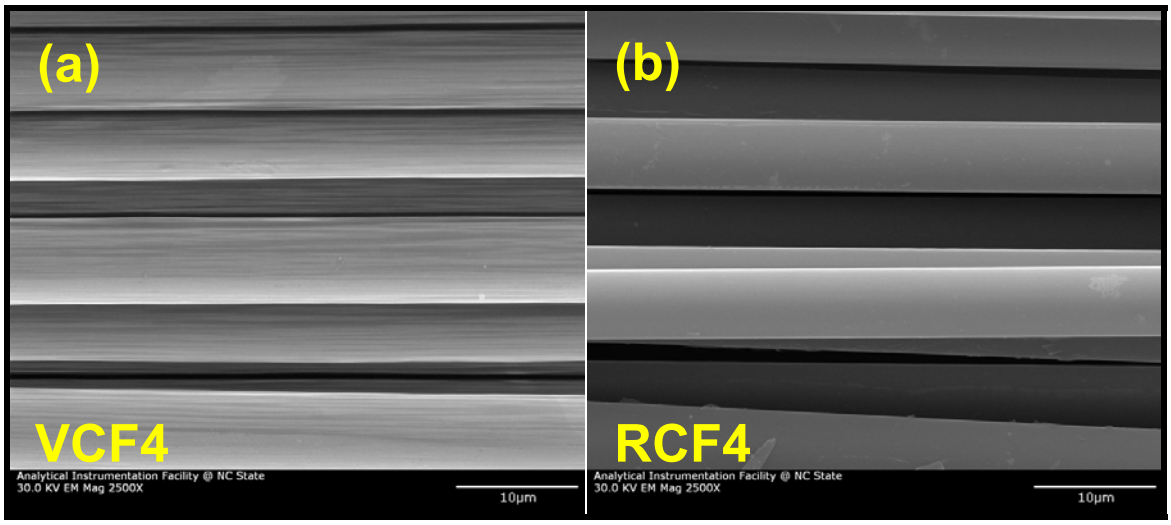

Figure 93 – Variable pressure SEM micrographs at 2,500X magnification for fiber sets (a) VCF4 and (b) RCF4

The field emission SEM helps reveal the striations present for both fiber samples at 5,000X magnification in Figure 94. These fibers exhibit similar morphology when compared at this magnification. Slight residue is present on RCF4 as well.

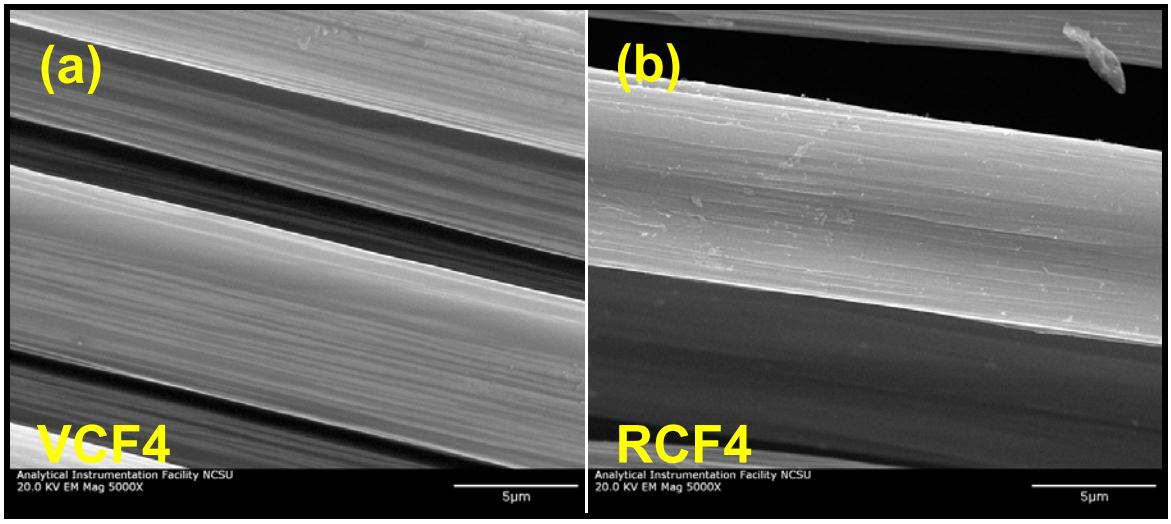

Figure 94 – Field emission SEM micrographs at 5,000X magnification for fiber sets (a) VCF4 and (b) RCF4

Again, at 10,000X magnification the two fibers have similar morphologies. It almost seems in Figure 95b that RCF4 has a twisted morphology, yielding striations with slight curvature. Furthermore, some particulates are present on the surface of the fiber, and it is not as clean as VCF4 at this magnification.

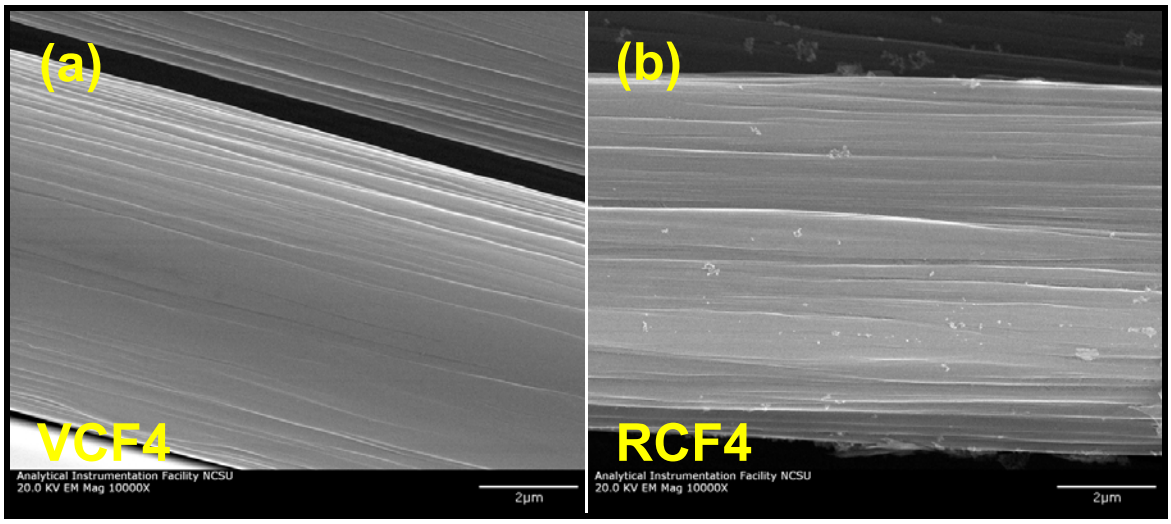

Figure 95 – Field emission SEM micrographs at 10,000X magnification for fiber sets (a) VCF4 and (b) RCF4

At 20,000X magnification, the recycled fiber sample still contains deep striations as does the virgin sample in Figure 96. Again, looking at the top of Figure 96b, it seems RCF4 has a twisted morphology. However, this could be another fiber in the background of the micrograph.

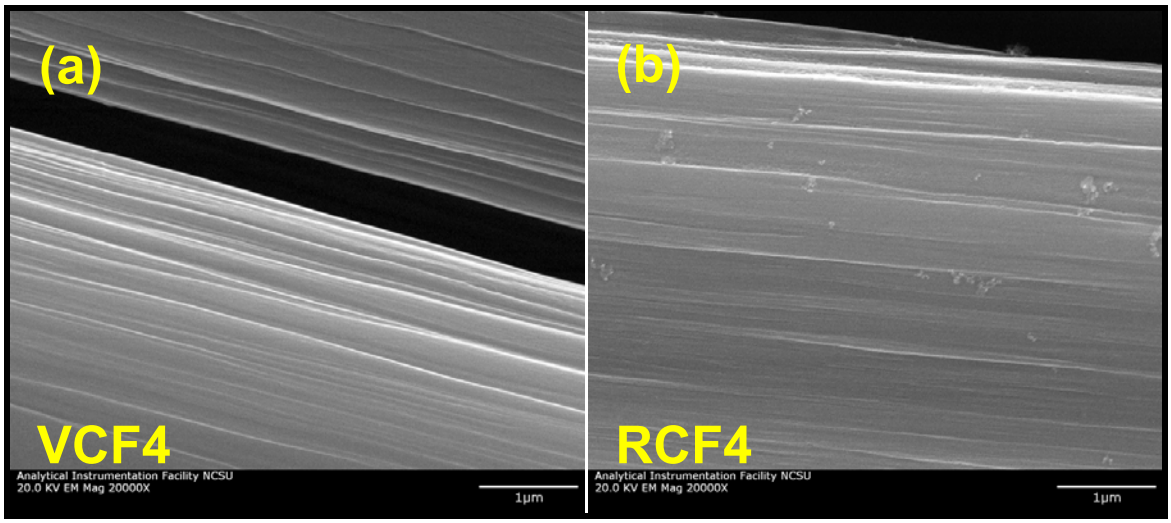

Figure 96 – Field emission SEM micrographs at 20,000X magnification for fiber sets (a) VCF4 and (b) RCF4

8.3 Fiber Diameter Measurements

Multiple fibers on two SEM micrographs for each fiber set were used to calculate the average fiber diameters. Over twelve fiber diameters were calculated for each individual fiber set at 5,000X magnification. Figure 97 shows typical measurements found for a fiber set (in this case RCF1).

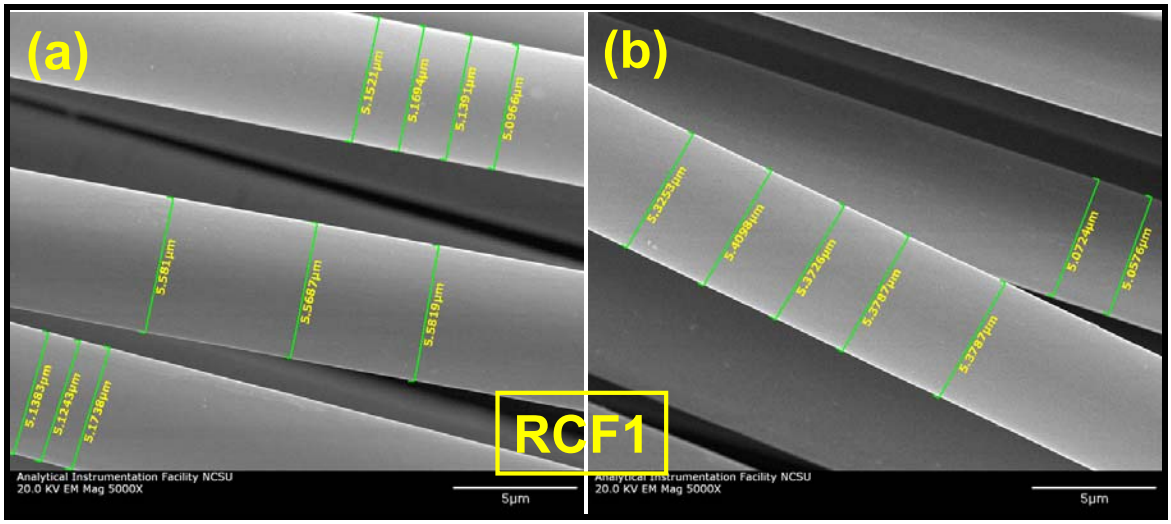

Figure 97 – Typical fiber diameter measurements for a fiber sample set (e.g., RCF1)

The average fiber diameter was calculated for all 8 fiber samples and tabulated in Table 26. The results indicate there was negligible change for all of the four samples: CF1, CF2, CF3 and CF4. A 7.44% increase in the fiber diameter from VCF1 (5.24 μm) to RCF3 (5.63 μm) occurred. However, this is still only a slight increase. The recycling processes performed by Milled Carbon Ltd. had little if any effect on the change in fiber diameter. Of the four sample sets, sample set CF3 had the largest difference. The other three recycled sample sets were derived from uncured carbon fiber, whereas RCF3 was derived from reclaimed part trimmings formed in a cured composite.

Table 26 – Average fiber diameter measurements for the 8 fiber samples

Fiber Set	**VCF1**	**RCF1**	**VCF2**	**RCF2**	**VCF1**	**RCF3**	**VCF4**	**RCF4**
Average Fiber Diameter (μm)	**5.24**	**5.28**	**6.60**	**6.35**	**5.24**	**5.63**	**7.23**	**7.52**
Standard Deviation (μm)	0.10	0.18	0.17	0.18	0.10	0.16	0.25	0.32
Percent Difference of Avg. Diameters	**0.76%**		**3.79%**		**7.44%**		**3.86%**	

Furthermore, the fiber diameters of the virgin samples were very similar to manufacturers' diameters listed in the technical data sheets. It is likely the companies rounded their fiber diameters for simplicity. Table 27 confirms the data provided in the technical data sheets.

Table 27 – Fiber diameter measurements comparing literature values to measured values

Fiber Diameter	VCF1 (Toray T800SC 24K)	VCF2 (Toray T700G 12K)	VCF4 (Cytec T300 3K)
Literature (μm)	5	7	7
Measured (μm)	5.24	6.60	7.23

8.4 Single Fiber Tensile Testing

Two sets of carbon fibers were exposed to single fiber tensile testing at Cornell University (Ithaca, NY) to reveal the mechanical properties of the single filaments. The two sets of fibers were CF1 and CF4 (both virgin and recycled were tested). The single fiber mechanical properties were compared at varying gauge lengths. For each gauge length, 50 fiber specimens were tested. All tests were performed at a strain rate of 0.4 mm/min on an Instron universal tensile tester (Model 5566). The tensile stress of the fibers was found along with the Weibull parameters α and β.

Two Weibull parameters, found through statistical analysis, were used for determining the failure of the single fibers. The Weibull shape parameter, β, indicates whether the failure rate is increasing, constant, or decreasing. A β value greater than 1.0 represents an increasing failure rate. The Weibull characteristic life parameter, α, indicates the scale/spread in the distribution of the data. The value of α equals the tensile stress that 37% of the fiber has exceeded. Table 28 and Figure 98 reveal the summary of the data collected for fiber sets CF1 and CF4.

Table 28 – Single fiber tensile testing data of Boeing 787 Dreamliner manufacturing CF scrap

Carbon Fiber / Property	Gauge Length (mm)	Tensile Stress (GPa)	Coefficient of Variation (%)	Scale Parameter, α (GPa)	Shape Parameter, β
VCF1	20	2.79	25.99	3.07	4.09
	50	2.20	36.94	2.46	2.74
	100	2.08	25.58	2.48	3.78
RCF1	20	2.48	22.08	2.70	4.71
	50	2.31	21.52	2.51	5.18
	100	2.31	22.15	2.51	5.14
VCF4	20	4.62	23.52	5.04	4.53
	50	3.28	31.09	3.64	3.66
	100	2.68	26.45	2.95	4.12
RCF4	20	2.43	24.65	2.66	4.53
	50	2.28	29.30	2.52	3.96
	100	1.70	33.14	1.89	3.41

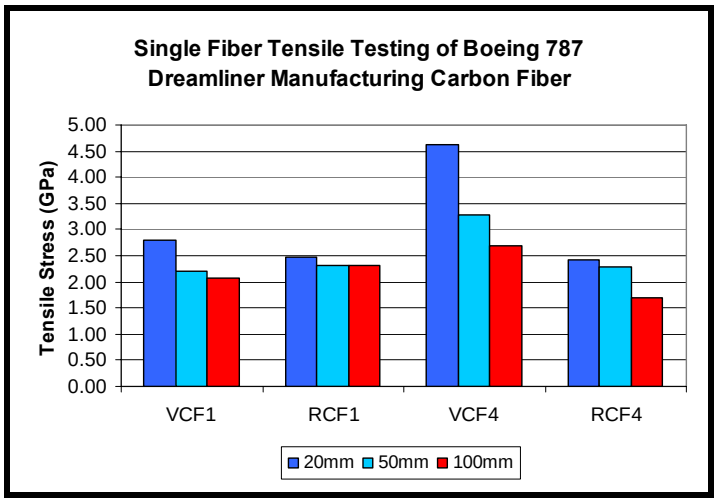

Figure 98 – Single fiber tensile testing data of carbon fiber derived from Boeing 787 manufacturing materials

Table 28 reveals RCF1 performed quite favorably compared to VCF1. This fiber set actually outperformed VCF1 when using the 50mm and 100mm gauge lengths. This is promising evidence that carbon fibers derived from manufacturing scrap can at times retain all their tensile strength compared to their virgin counterparts. However, RCF4 clearly had

diminished mechanical properties compared to the virgin fiber VCF4. RCF4 retained anywhere from about 50% to 70% of its strength compared to VCF4 depending on gauge length. The 20mm gauge length yielded fibers which were very poor compared to the virgin material. Only 50% strength retention is not promising.

As the gauge length increased, the fibers exhibited a trend of decreasing tensile strength. This behavior was consistent with all of the fibers tested. The virgin fibers were also compared to the single fiber tensile testing data the manufacturers reported. The Toray VCF1 and Cytec VCF4 are reported to have a tensile strength of 5.88 GPa and 3.75 GPa respectively. These are two separate companies, which might have used different experimental procedures. The two main variables most likely manipulated are the strain rate and the gauge length used. VCF1 exhibited its highest tensile value of 2.79 GPa at 20 mm. This value is considerably lower than the reported 5.88 GPa value by Toray. It is possible that Toray used a gauge length less than 20 mm to achieve such a significantly higher value. VCF4 actually outperformed the manufacturer's data at 20 mm by about 20%. Again, Cytec could have used a gauge length between 20 and 50 mm to achieve their tensile value.

8.5 X-ray Photoelectron Spectroscopy

The same experimental procedure used on the carbon fiber derived from the A-03 CFRP was performed on the Boeing 787 material. Two specimens were tested from CF1 and CF4 to gather an average elemental composition on the surface of the carbon fibers. The data for the CF1 and CF4 sets are shown in Table 29 and Table 30 respectively. Table 29 reveals the virgin fiber set (VCF1) did not have nitrogen or silicon present on the surface of

the fibers, whereas RCF1 contained an average of 2.61% and 1.04% of nitrogen and silicon respectively. A considerably larger amount of carbon was present on the surface for RCF1 compared to VCF1.

Table 29 – Overall elemental atomic percentages present in the XPS scan for CF1 sample set

Element/Sample	VCF1-1	VCF1-2	Avg. VCF1	RCF1-1	RCF1-2	Avg. RCF1
C 1s	71.28	71.53	71.41 (0.18)	81.96	79.80	80.88 (1.53)
O 1s	28.72	28.47	28.60 (0.18)	15.13	15.81	15.47 (0.48)
N 1s	0.00	0.00	0.00 (0.00)	2.91	2.31	2.61 (0.42)
Si 2p	0.00	0.00	0.00 (0.00)	0.00	2.08	1.04 (1.47)

Nitrogen was much more prevalent in both fiber sets from CF4. VCF4 and RCF4 contained an average nitrogen concentration of 3.21% and 8.64% respectively. These percentages are considerably larger than the CF1 fiber set. Silicon was not present on VCF4 or RCF4. Again, the recycled carbon fiber (RCF4) contained a higher amount of carbon on the surface of the fibers than the virgin fiber sample (VCF4).

Table 30 – Overall elemental atomic percentages present in the XPS scan for CF4 sample set

Element/Sample	VCF4-1	VCF4-2	Avg. VCF4	RCF4-1	RCF4-2	Avg. RCF4
C 1s	69.73	70.28	70.01 (0.39)	73.64	78.19	75.92 (3.22)
O 1s	26.67	26.92	26.80 (0.18)	15.86	15.05	15.46 (0.57)
N 1s	3.61	2.80	3.21 (0.57)	10.51	6.76	8.64 (2.65)

The average values for all of the elements present in the overall scan of the four carbon fiber samples are summarized in Figure 99. Again, carbon is the most prominent element present on the surface of the carbon fibers.

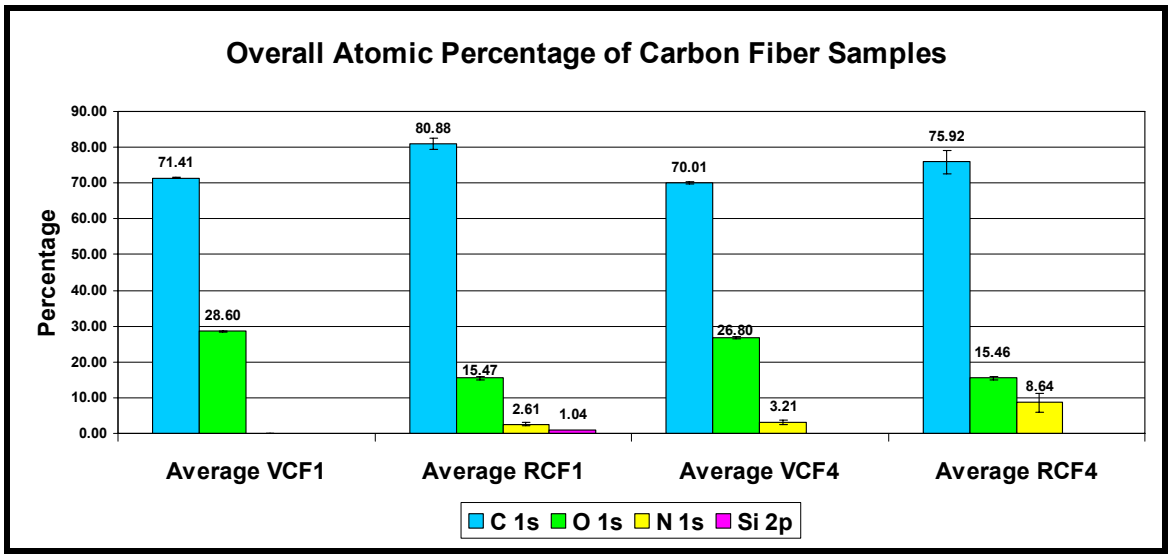

Figure 99 – Overall atomic percentages on the surface of the carbon fiber samples

Throughout literature, atomic ratios are calculated for the elements present, usually including carbon, oxygen, and nitrogen. These ratios were calculated and summarized in Table 31. Again, literature reveals the higher the oxygen percentages, the better the resin to fiber adhesion. Therefore, simply using the data compiled from the overall scan of the carbon fiber surfaces, the higher the O/C ratio, the better the expected adhesion of the fiber to the resin. The O/C ratios show the virgin fibers have almost double the ratio of their recycled counterparts. Sizing on the virgin fibers is the cause of this behavior.

Table 31 – Atomic ratios calculated from the surface atomic percentages of the overall scan

Ratio	VCF1	RCF1	VCF4	RCF4
O/C	0.40	0.19	0.38	0.20
N/C	0.00	0.03	0.05	0.11
(O+N)/C	0.40	0.22	0.43	0.32

Deconvolution of the carbon peak is also helpful for determining how the fiber will bond to the resin. It is clear in Figure 100 there is considerably less C-C graphitic bonding in the virgin fibers. The C-O hydroxyl and C=O carbonyl bonding is considerably higher for the virgin fibers compared to the recycled fibers. This is due to the sizing present on the surface of the virgin carbon fibers. This sizing is used to better adhere the carbon fibers to the polymer resin. Future work should remove the sizing by performing a soxhlet extraction so that the virgin carbon fibers could be more directly compared to the recycled fibers.

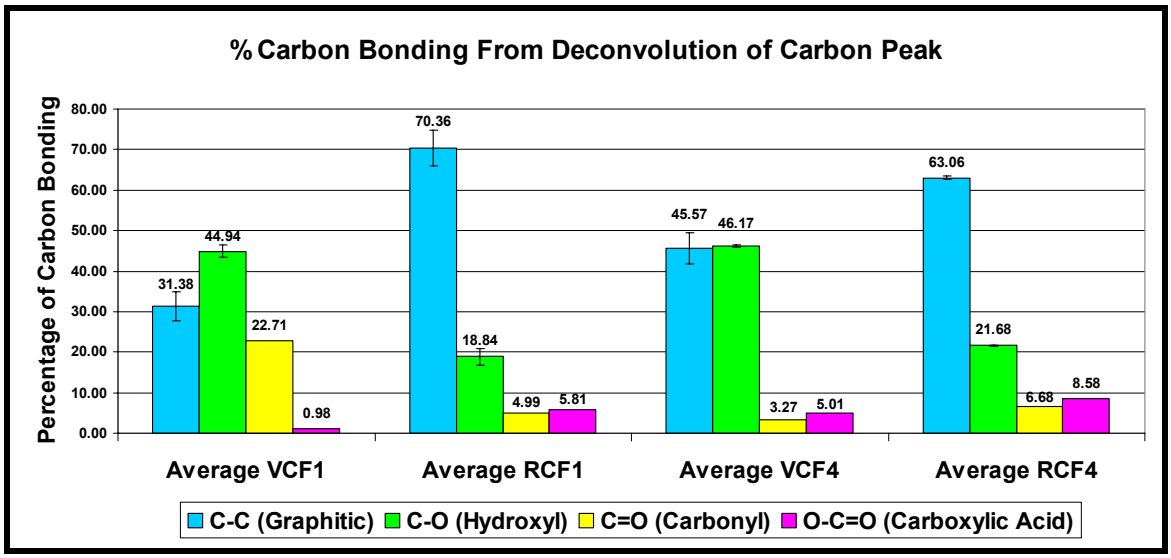

Figure 100 – The deconvolution of the carbon peak to determine the percentage of carbon bonding

A representative scan is shown for the four carbon fibers in Figure 101 to Figure 104. The overall atomic scan of the surface is shown in Figure Xa, whereas the deconvolution of

the carbon 1s peak is shown in Figure Xb. The different functionalities are imposed on the overall curve. Figure 101 and Figure 103 have shoulders on the C 1s peak indicating sizing present for VCF1 and VCF4 respectively.

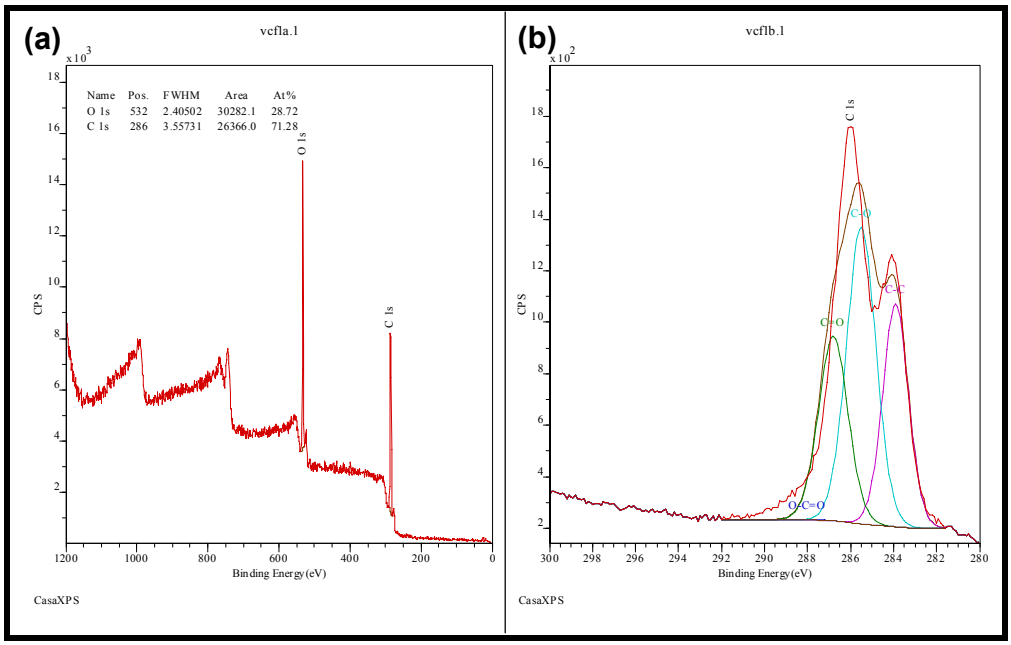

Figure 101 – Representative XPS data of VCF1 for (a) overall atomic percentages on surface, (b) deconvolution of carbon peak

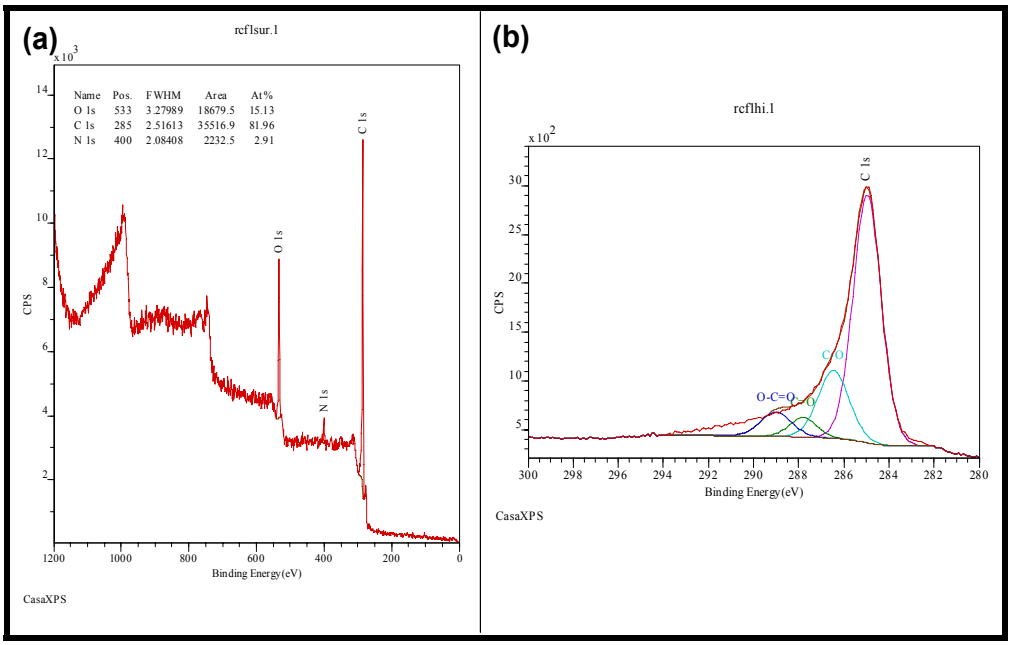

Figure 102 – Representative XPS data of RCF1 for (a) overall atomic percentages on surface, (b) deconvolution of carbon peak

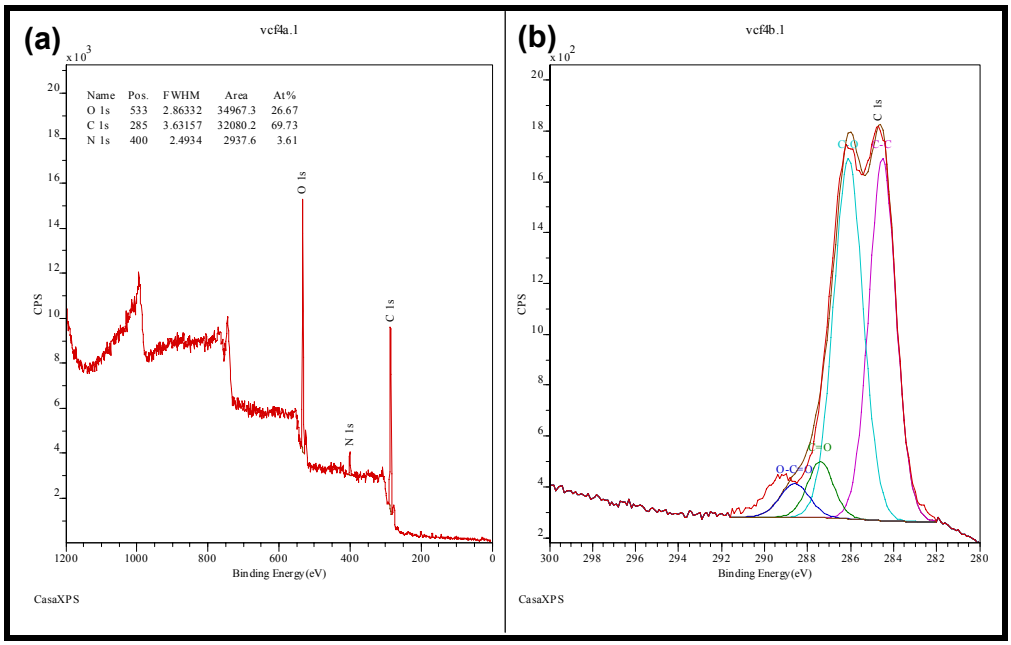

Figure 103 – Representative XPS data of VCF4 for (a) overall atomic percentages on surface, (b) deconvolution of carbon peak

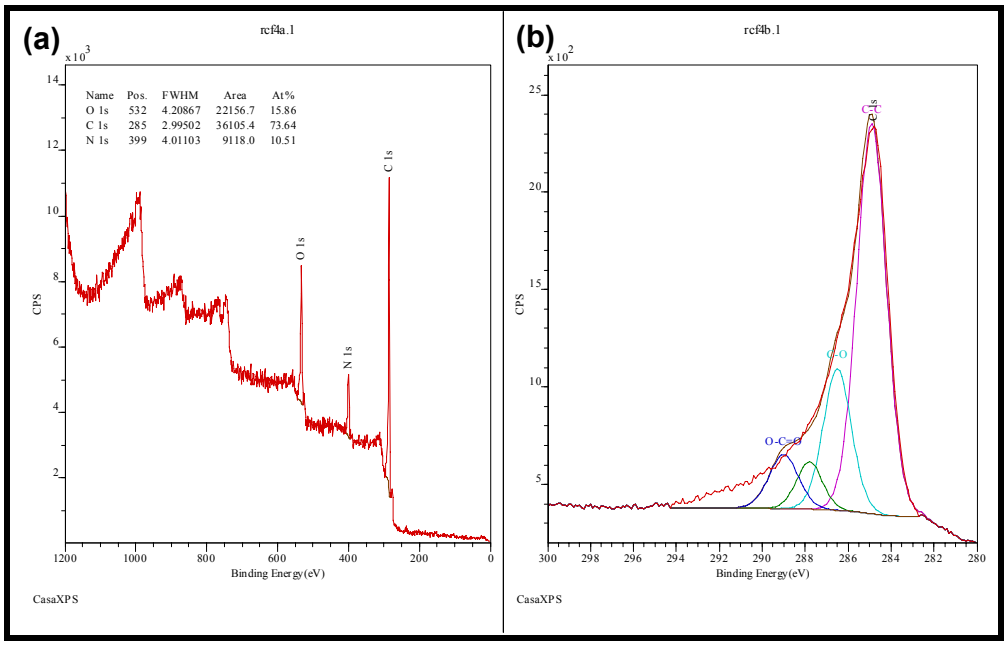

Figure 104 – Representative XPS data of RCF4 for (a) overall atomic percentages on surface, (b) deconvolution of carbon peak

8.6 Conclusions

The recycled carbon fiber derived from the Boeing 787 Dreamliner's manufacturing scrap is considerably cleaner than RCF recovered from EOL scrap as revealed in scanning electron micrographs. Also, the recycled fibers, in one case (RCF1), outperformed the virgin material with respect to single fiber tensile testing. This behavior is very promising for integration of recycled carbon fibers back into polymer matrices. However, RCF4 only exhibited 50% to 70% strength retention. A soxhlet extraction must be performed on the virgin fibers to better compare the recycled and virgin fibers' surface functionalities. This will be helpful in determining how the recycled fibers behave when integrated with a new polymer. For better integration into new polymer matrices the recycled fibers could be exposed to a sizing for improved fiber/resin adhesion. Overall, the fibers derived from the manufacturing scrap seemed very comparable to the virgin material and would be the easiest

feedstock to implement into new composite parts.

9. Overall Conclusions

Carbon fiber reinforced plastics are becoming mainstream engineering materials. Various industries, especially the aerospace sector, are using increased amounts of carbon fiber composites. With this surge in material use, waste is constantly accumulated. Currently, manufacturing waste and end-of-life composite material is being landfilled. A need for recycling composites has arisen, and technologies have been developed to recover the carbon fibers from the composite waste. This research has proven through an array of characterization techniques, that recycled carbon fibers still retain much of their inherent value (both the mechanical and surface properties) compared to virgin carbon fibers.

After characterizing the promising properties of recycled carbon fibers, they were then successfully reintroduced into new composites. The thermoset resins used were epoxies, vinyl esters, and phenolics. Existing composite fabrication techniques were used, such as VARTM, BMC, and compression molding, to manufacture composite panels for mechanical testing. Overall, the testing proved the R-CFRPs did not retain much strength compared virgin CF reinforced composites. However, in some cases, the R-CFRPs showed promise for use as reinforcement in various composite applications, exploiting specific mechanical properties. The main theme, however, is that composites were formed by successfully integrating recycled carbon fibers into new polymer resins.

Another successful proof of concept was the fabrication of a 3-D part using a bulk molding compound. A fuse box cover panel was fabricated using recycled carbon fibers as

reinforcement material. This achievement showed actual parts can be manufactured using this recycled material.

Furthermore, recycled carbon fibers were characterized from manufacturing scrap derived from the Boeing 787 Dreamliner, currently in production. The RCFs, in some cases, retained a majority of their strength compared to their virgin counterparts. Also, the surfaces of the fibers seemed extremely clean compared to RCFs derived from cured composite scrap. This research proves the proper recycling infrastructure/optimization will yield recycled carbon fibers which can be successfully implemented into new composite components and compete in multiple industry sectors and material applications.

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