CLOSED LOOP RECYCLING OF CFRP INTO HIGHLY ALIGNED HIGH PERFORMANCE SHORT FIBER COMPOSITES USING THE *TUFF* PROCESS

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ABSTRACT

Current Carbon (CF) Fiber Reinforced Polymers (CFRP) recycling strategies reclaim continuous CF in powder or short fiber form. The material is added to molding compounds as a filler or short fiber reinforcement having random or semi-aligned orientation to produce composites with low fiber volume fraction and reduced mechanical properties (down cycling). Down cycling reduces the value chain limiting the recycling opportunities of CFRPs. This paper combines a short fiber alignment process (*TuFF*) with 1) the use of low-cost, short CFs obtained from recycled and waste stream, and 2) recycling of *TuFF* material using thermolysis to produce highly aligned short fiber composites with mechanical properties approaching continuous fiber levels. The closed-loop process recycles the CFRP, reclaims the fiber content, aligns the fibers using the *TuFF* process and produces new CFRP components with high property retention. The method reduces material and part cost and allows true recycling and reuse of CF components into high-performance parts.

1. INTRODUCTION

The CF industry has grown significantly over the last decade. In 2000, the global market for CFRP was less than 20,000 tons annually and has been growing by a factor of three today with a forecast to reach 140,000 tons in the early 2020s [1]. This growth combined with new government regulation raises questions on the importance of CF recycling in the further growth of the composite market. Recycled CF products can reduce the cost of light weighting particularly in high-volume applications (such as demonstrated in the BMW i3 and i8 program). From an environmental standpoint, reducing CF waste with its high embedded energy through recycling is energy-efficient and a legislative requirement in many countries. Ultimately, the drive for consumer applications to be "green" as part of industry social responsibility is a key driver to incorporate recycling strategies in composites end-use applications.

Nevertheless, recycling of carbon fiber composites is in its infancy as an industry in the US, with promising technologies such as Solvolysis, Pyrolysis and Thermolysis being developed through partnerships between small businesses and large OEMs in both the US and Europe [2]. Materials Innovation Technologies (MIT, Fletcher, NC) now Carbon Conversions Inc. mechanically shreds the CFRP into smaller pellets, pyrolyzes the pellets and then converts the short fibers into preforms or rolled goods. Adherent Technologies, Inc (Albuquerque, NM) is using a mechanical process to reduce the material to coupon size followed by wet chemical degradation of the polymer matrix to separate the polymer from the fiber form. Adherent licenses and sells complete plant installations of their process. In Europe, other recycling vendors (ELG Carbon Fibre, CFK Valley Stade Recycling GmbH) are using similar technical approaches to recycle CFRP waste (Figure 1).



Figure 1: Discontinuous chopped fibers and short fiber random mats are producible both from manufacturing scrap (including cured and uncured prepregs) and from end-of-life composite products [2]

All these competing technologies provide the recycled carbon fiber in discontinuous chopped or short fiber random & semi-aligned form, which results in reduced mechanical properties that can be achieved in the composite parts using current processing methods. For example, tensile strength of MIT's DEP recycled preforms (156MPa with fiber length distribution between 6-25mm) molded with polyester [3] is ~20% compared to an equivalent continuous carbon fiber quasi-isotropic prepreg composite at 50% fiber volume fraction while the resultant tensile modulus fiber translation is 50% (22GPa). This is mainly due to the random fiber orientation and low fiber loading of the preform and reduced fiber and adhesion properties of the recycled fibers. The TuFF program has demonstrated property translation of ~2700MPa (strength) and 160GPa (modulus) within an aligned short fiber unidirectional composite and virgin fiber processed in an autoclave which is almost 100% property translation for both strength and modulus of an equivalent continuous prepreg part. The new aligned material form is called Tailorable Universal Feedstock for Forming (*TuFF*) and is discussed in more detail in the literature [4]. This paper discusses a closed-loop process where the CFRP part is recycled, fiber content is reclaimed, followed by fiber alignment using the *TuFF* process and fabrication of a new CFRP components with high property retention. The method reduces material and part cost and allows true recycling and reuse of CF components into high-performance parts for the first time.

2. EXPERIMENTATION

The *TuFF* process is fiber and resin agnostic and produces a highly aligned fiber preform which can be further impregnated with the polymer using film infusion or liquid molding techniques. Virgin unsized continuous carbon tows were cut to provide a controlled short fiber material for process and property evaluation. The fibers were aligned with the *TuFF* process as a thin ply sheet and infused using an infusable resin system to create a unidirectional part to baseline the mechanical properties and as feedstock for the pyrolysis step. The recycling step recovered the fiber material (additionally, the polymer content can be fully recovered but that was not a focus of this paper) and reintroduced into the *TuFF* process producing a part with the recycled fibers. Mechanical and other property tests were conducted to compare the virgin material properties with the recycled material after one cycle. The recycling process can be repeated as long as fiber and CFRP material properties meet the performance metric as defined by application. Figure 2 outlines this recycling process.

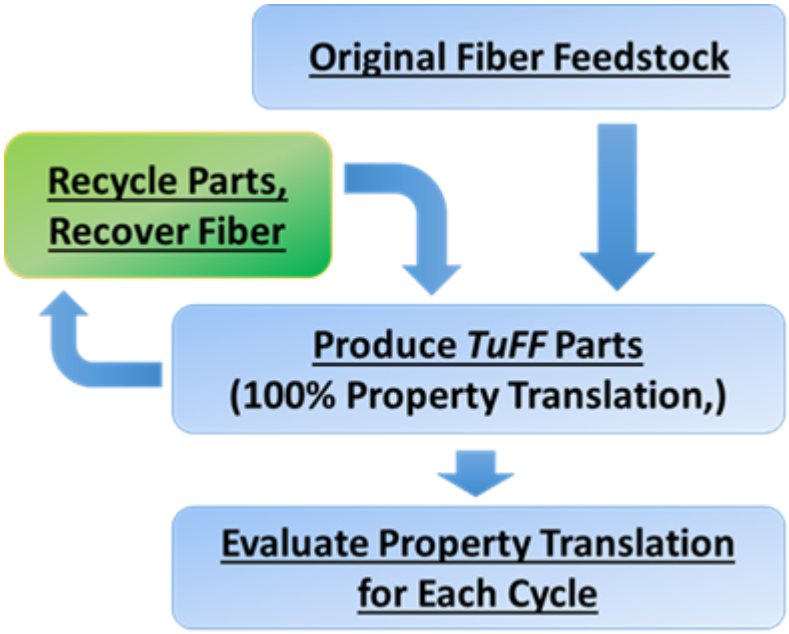


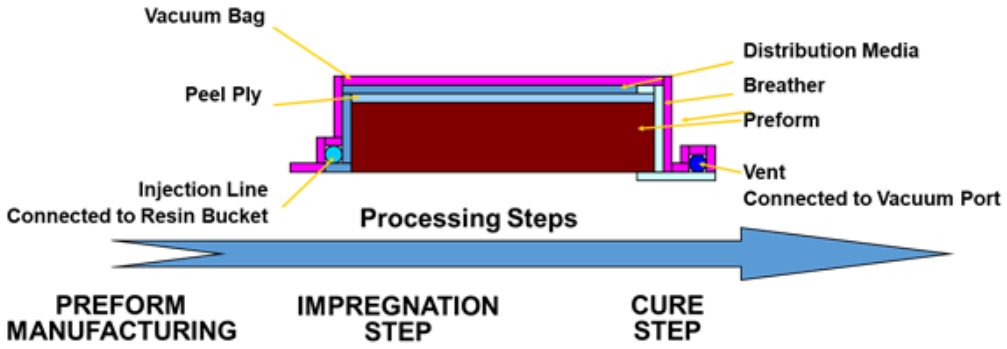
Figure 2: Our approach demonstrates technical feasibility of closed loop recycling of CFRP using *TuFF*

2.1 Materials and Process

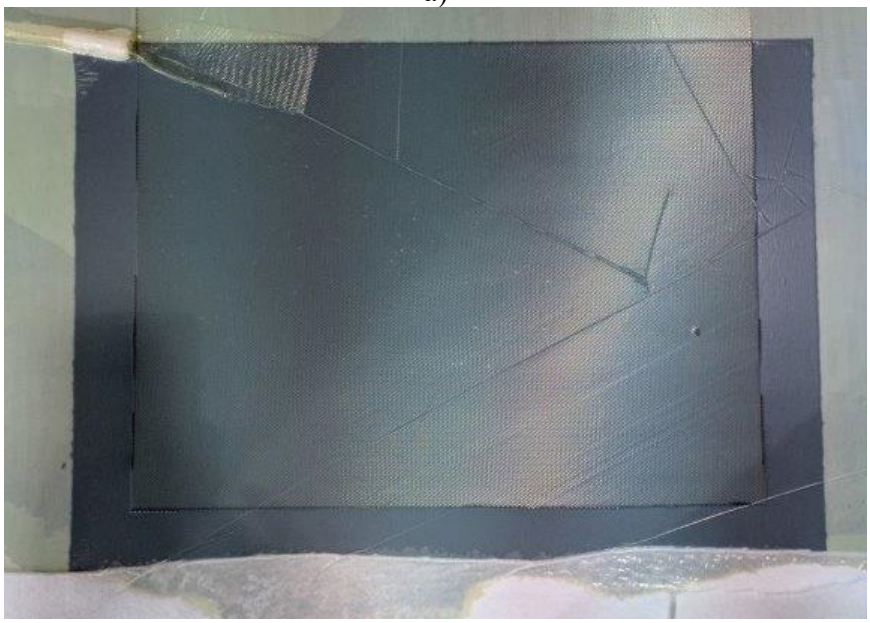
The fiber properties and fiber length distribution are critical material parameters for full tensile translation in short fiber composites. Ongoing work conducted at UD-CCM demonstrated 100% tensile strength translation with a 3mm unsized IM7 carbon fiber in a PEI thermoplastic matrix [4]. The same fiber material was used as a starting material to create baseline material properties for this effort. The fiber length was characterized and compared before and after recycling iterations to quantify fiber length degradation. Other parameters such as fiber strength retention after recycling or the interfacial properties were not evaluated in this paper but may affect final properties and will be a focus of future work.

Arkema recently introduced an infusible thermoplastic polymer called Elium which demonstrated good performance in crashworthy automotive parts [5]. Elium 150 is a low viscosity acrylic resin with mechanical properties similar to epoxy while presenting the advantages of being post-thermoformable and recyclable [6]. The starting viscosity is approximately 100 mPas with a gel time of about 30 minutes at room temperature. Other Elium types are commercially available and are optimized for pultrusion, RTM and hand-layup.

TuFF dry preforms of about 200gsm were assembled and infused at room-temperature using the Elium resin as shown in Figure 3. Full resin penetration of the reinforcement was visually observed and the part was demolded and prepared for microstructural and mechanical property evaluation.



a)



b)

Figure 3: a) Schematic of a typical VARTM setup, and b) Infused *TuFF* sample showing plumbing, distribution media and breather setup

2.2 Pyrolysis

Pyrolysis in an argon atmosphere was chosen for the fiber reclamation process. The Elium resin is suited for pyrolysis since, unlike epoxy-based resins, the pyrolysis process depolymerizes

Elium resin completely, leaving no ash [7]. This complete depolymerization is ideal for reclaiming the fiber since no residue is left in the fiber bundle or on the fiber surface. Residue can cause the fibers to stick together, making recycling more difficult, or inhibit good adhesion with resins, thus is undesirable for fibers intended for recycling using the *TuFF* process. Additionally, the relatively low temperature for pyrolysis minimizes fiber degradation while keeping energy cost low.

In this study, the composite samples were placed into a crucible and then into the furnace. A continuous supply of argon gas was pumped into the furnace to produce an inert atmosphere, thus preventing any oxidation of carbon fiber. The furnace was heated at 5°C/min to 350°C and held for 60 minutes followed by another heating ramp at 5°C/min to 400°C and held for 180 minutes. The samples were then allowed to cool naturally in the furnace. Figure 4 shows the resulting *TuFF* fiber material on a metal mesh. The depolymerization process has not had any significant effect on the alignment of the 3mm short fiber and could be used directly as a preform for the second infusion. To demonstrate the more general case of recycling, the preform is randomized and dispersed prior to re-alignment in the *TuFF* process, re-infusion and property determination.



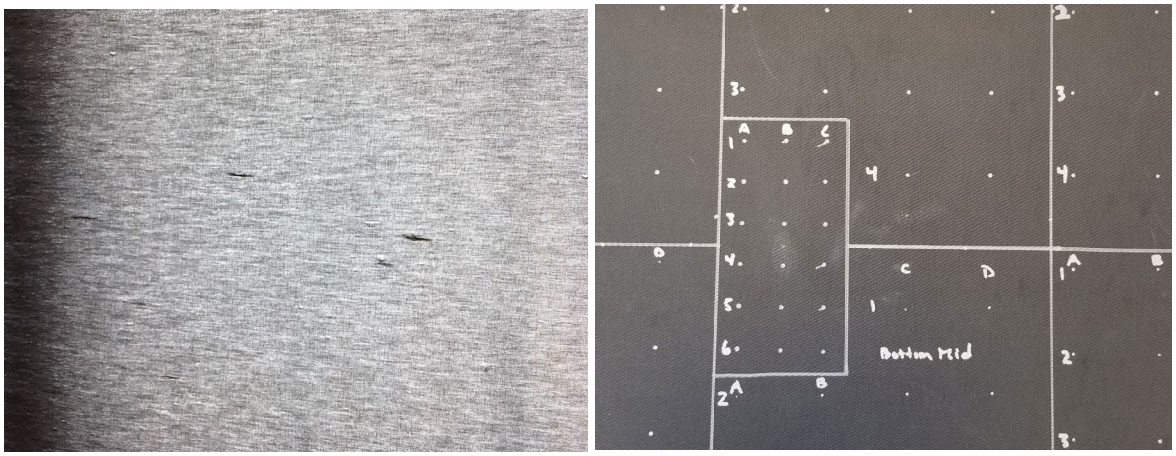
Figure 4: Recovered fiber material after pyrolysis

The pyrolysis process was successful in removing the Elium matrix out of the composite, allowing for the recycling of the fiber and the fabrication of an all-recycled-fiber *TuFF* composite panel. However, the effects of the pyrolysis on the fiber strength and surface chemistry is not addressed in this paper. This study addresses fiber attrition in the form of fiber length distribution through the fiber lifecycle at each of the recycling and forming steps. The pyrolysis process may change the surface chemistry, wetting characteristics and level of fiber-matrix adhesion. The potential changes in surface chemistry and surface energy due to the pyrolysis process will ultimately affect the effectiveness of the fiber reinforcement and therefore become important as the recycling process is repeated. A study similar to that found in Deitzel et al. [8] will be conducted to investigate the changes in fiber strength, surface chemistry, and their effects on fiber-matrix interface strength. Furthermore, the thermal oxidation technique found in

that study can easily be adopted to clean and re-oxidize the recycled fiber surface to improve wetting and adhesion without fiber strength degradation.

3. EXPERIMENTAL RESULTS

This study evaluates fiber length degradation due to the *TuFF* and recycling process, part quality through microstructure evaluation and ultrasonic C-scans, as well as tensile properties of the CFRP before and after the recycling process. Original fibers were aligned using the *TuFF* process and then infused via the VARTM process. Samples for mechanical testing and microstructure evaluation were cut and the remaining material pyrolyzed. Fibers from the recycled sections were reintroduced into the *TuFF* alignment process, (see Figure 5a) and a panel from the recycled fibers was infused. The recycled fiber panel size (see Figure 5b) was slightly smaller (600mm x 450mm original fiber panel; versus 550mm x 350mm recycled fiber panel) as the small amount of excess material used during start and stop of the alignment process was not reused to make the recycled mechanical test panel in this study. This excess material, however, can be recycled within the alignment process and fully used without any limitations. Visual inspection of the aligned *TuFF* material after recycling showed a small amount of fiber clumps, where the standard alignment process conditions did not fully separate these fibers (some process optimization may be required to eliminate this clumps during recycling iterations). This could also be due to some resin remaining on the fiber that stick together as micro-tows. This will be evaluated in future efforts using SEM and microscopy that could lead to changes of the pyrolysis step to ensure full loss of the resin with full dispersion in the *TuFF* process.



a) b)

Figure 5: a) Aligned *TuFF* sheet shows a small amount of conglomerated recycled fibers and b) infused part shows full impregnation of the recycled *TuFF* preform

3.1 Fiber Length Degradation

Fibers were dispersed through mild mixing in an ethanol 200 proof in order to perform fiber length measurements. This minimized energy to separate the fibers and avoided fiber breakage during the measurement step. Several pictures were taken with a CCD-camera with a resolution of 2592x1944 pixels. Individual fibers were manually marked and length measured using Image J software. Figure 6 shows the dispersed recycled IM7 fibers, and several marked fibers identified for length measurement. A minimum of 200-250 fibers were measured to provide an

accurate statistics of the fiber length distribution. Bias was avoided by measuring each fiber in the picture except edge fibers continuing past the image and the micro-tows.

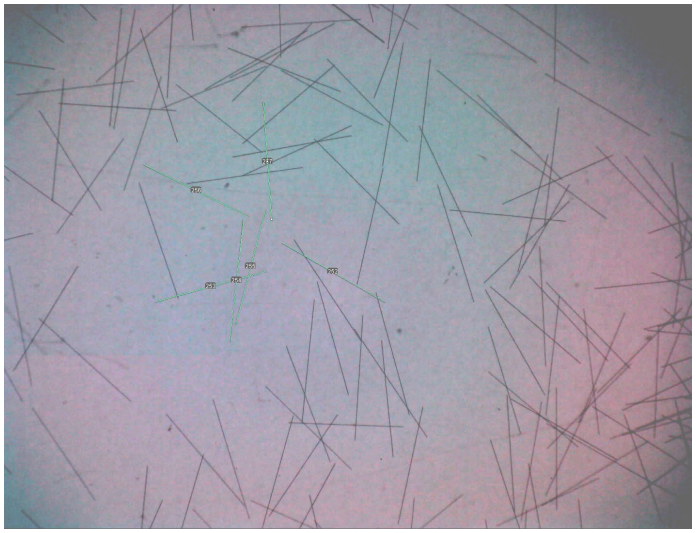


Figure 6: Fiber Length measurements of recycled IM7 fibers after fiber dispersion in ethanol 200

Figure 7 and Table 1 show the results of fiber length measurements of the original cut IM7 fiber (baseline), after initial alignment, after the first pyrolysis, after the second alignment step and once again after second pyrolysis. A *TuFF* fiber patch was separated from the preform to measure the fiber length after alignment, while a small amount of fibers were taken with a tweezer from the recycled fiber material. A slight shift of the distribution is observed from the baseline data compared to all subsequent datasets. The origin is not clear, but a small amount of fiber breakage during initial mixing and alignment is possible. A statistiscal significant length change is observed after the second pyrolysis step. Slightly higher number of fiber micro-tows is observed and has to be separated during dispersion, which may have led to the increase in smaller fiber count. The pyrolysis step has to be optimized to ensure full removal of Elium at each iteration. The overall effect of fiber breakage can be assessed through mechanical property measurements.

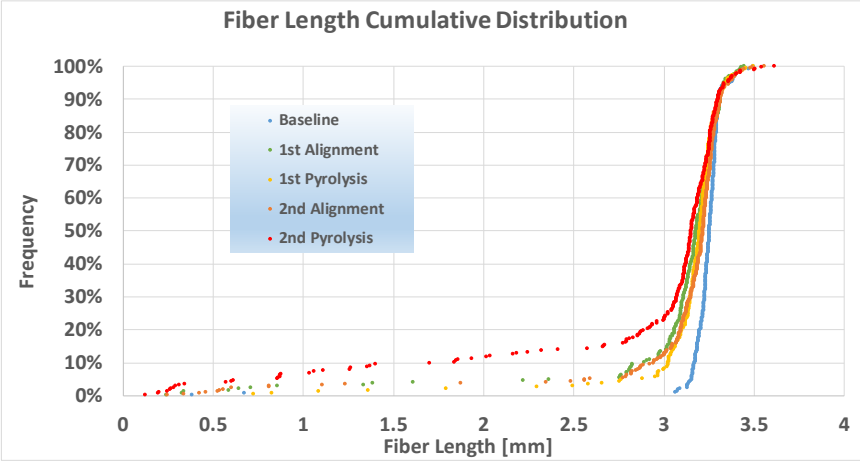


Figure 7: Fiber length results after *TuFF* alignment and pyrolysis shows only small length degradation

Table 1: Fiber length measurements before and after pyrolysis

	Count	Average (mm)	Median (mm)	Standard Deviation (mm)	Coefficient of Variation
IM7 Baseline	274	3.23	3.25	0.31	10.0%
1st Alignment	235	3.06	3.18	0.55	17.9%
1st Pyrolysis	227	3.13	3.20	0.39	12.5%
2nd Alignment	338	3.09	3.22	0.53	17.1%
2nd Pyrolysis	271	2.88	3.15	0.79	27.4%

3.2 Part Quality

The original and recycled fiber panels were ultrasonically scanned in through-thickness scan mode with a spatial resolution of 1mm. One 5MHz transducer is used to send with a second 5MHz receiver transducer receiving the transmitted signal after penetration through the composite panel. The signal amplitude is plotted in Figure 8, where any material attenuation is attributed to material (such as fiber content) or thickness variation, as well as defects such as voids or dry material. Overall, the ultrasonic scan looked uniform without significant areas of concerns. The average attenuation is 6.52dB ±0.65 dB for the original panel and 5.94dB ±0.66 dB for the recycled panel indicating a similar level of wet-out and resulting fiber volume fraction.

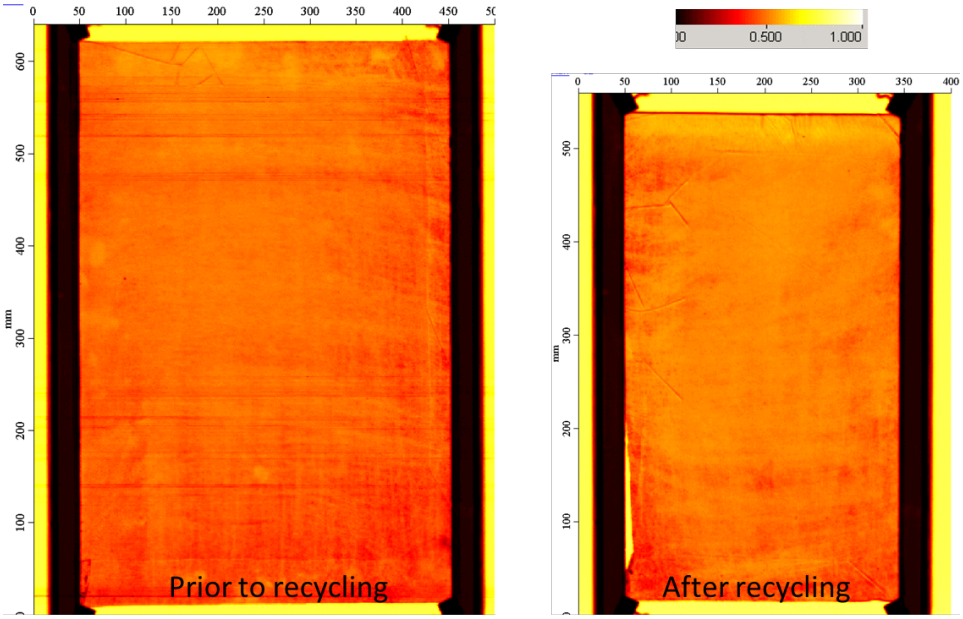
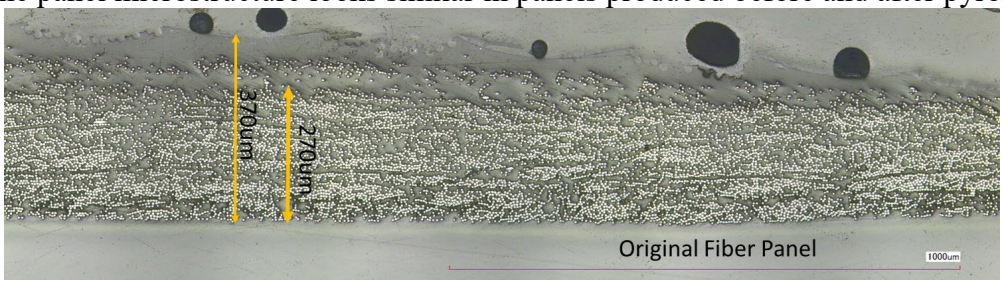


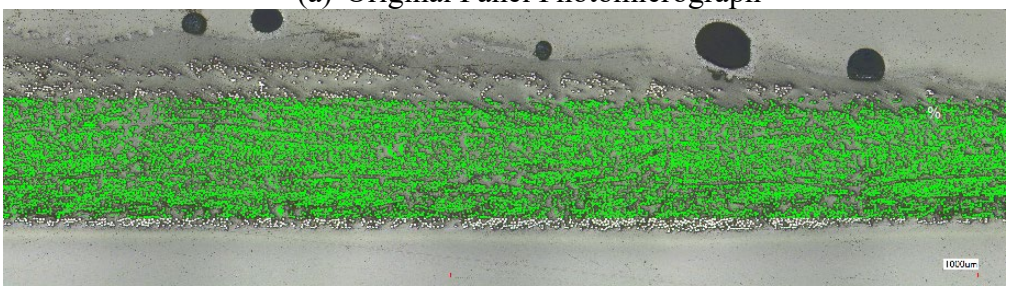
Figure 8: Ultrasonic C-scan of Panels produced before and recycling show no degradation or defects with the original and recycled fiber material

Samples from both panels were potted and microscopic images were taken with a VK-X200 3D Color Laser Scanning Microscope (Figure 9). Full impregnation of the resin into the reinforcement is observed with low void content measured below 1%. Any fiber misalignment will result in non-circular fiber features with only a couple of outliers shown, indicating good

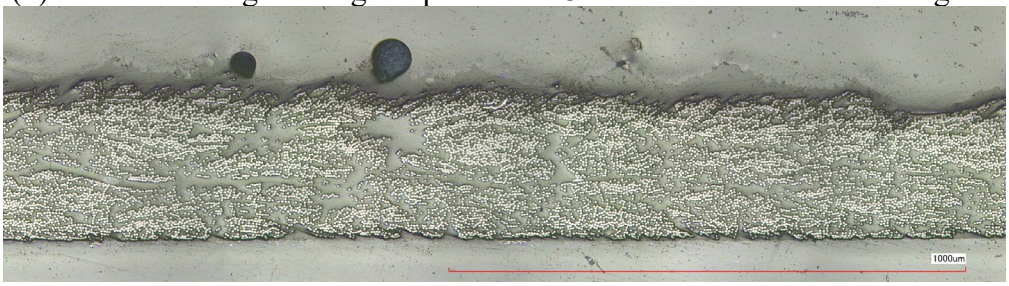
alignment of most fibers in both panels. The images illustrate an artifact of the VARTM process where the peel ply creates a resin-rich surface where fiber bridging occurs. In thin layers, this resin rich surface can lower the bulk fiber volume of the composite specimens. The high fiber volume bulk regions is approximately 270µm thick for both samples, while the resin rich layer contains only a small amount of fiber that adds to the coupon peak thickness ~100µm and 80µm for the original and recycled specimen, respectively. The image was analyzed using the SMARTree Image Analysis module that features windowed measurement of fiber volume fraction [9]. The fiber volume fraction was measured to be 31% Figure 9(b) in the high fiber volume fraction bulk section while only 27% if the full thickness is considered. The recycled fiber volume fraction Figure 9(d) was measured at 30%. Thicker panel constructions will reduce the effect of the surface and lead to higher fiber volume fraction parts. Future effort will fabricate standard thickness (1mm and thicker) coupons or use caul plates to eliminate any surface issues and higher compaction pressures will be used (only vacuum pressure was used in this study) Overall, the panel microstructure looks similar in panels produced before and after pyrolysis.



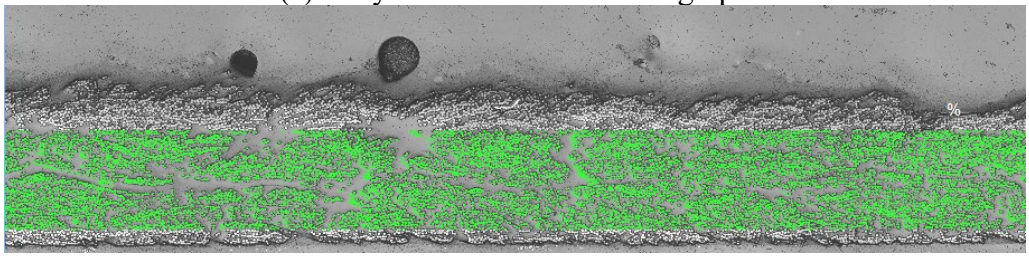
(a) Original Panel Photomicrograph



(b) Threshold image of original panel with 31% Fiber volume in bulk region.



(c) Recycled Panel Photomicrograph



(d) threshold image of recycled material with 30% fiber volume fiber in the bulk
Figure 9: Microscopic images show no discernable difference in the microstructure before and after the recycling step

3.3 Tensile Properties

Tension properties were measured for both the baseline and recycled panel by extracting sub-panels as shown in Figure 5. Panels were approximately 18cm x 10cm in dimension with the longer side along the zero degree fiber direction. ASTM D 3039 preparation methodology was followed with 3.8cm (1.5") tabs resulting in a gage section of approximately 7.5cm (3") with sample thicknesses as documented previously. Tension testing followed ASTM D 3039 guidelines for loading rates, with back-to-back bi-axial strain gages to identify any potential sources of asymmetry in the samples (i.e. resin rich surface layer). Longitudinal and transverse strains were calculated as the average of both gages, followed by data reduction per ASTM D 3039. Results from tension testing of the baseline and recycled panels are shown in the Table below. Future tests will evaluate thicker panels and at higher compaction pressure to retain a higher fiber volume fraction to improve overall mechanical properties.

Table 2: Comparison of 0 Tension performance of baseline and recycled *TuFF* composites

Panel	Strength [MPa]	Modulus [GPa]	Poissons Ratio	Strain [%]
Baseline	776 ± 40.6	72.6 ± 0.76	0.3 ± 0.01	1.08 ± 0.00
Recycled	765 ± 70.0	72.1 ± 1.52	0.33 ± 0.02	1.07 ± 0.00

A comparison of the mechanical performance shows average modulus, strength and strain to failure fall within the measured baseline statistics for the recycled system. There is no degradation in the average properties after recycling. However, variability in properties has increased in the recycled system, which may be attributed to the small amounts of micro-tows present in the recycled preforms prior to infusion (Figure 5). Micro-tows are possibly due to incomplete pyrolysis. Pyrolysis may also lead to reduced adhesion or more variability in adhesion on the fiber surface. Both mechanisms may lead to increased variability and will be investigated in future studies. Failure modes were typical of unidirectional carbon fiber tension samples, with explosive failure modes. Stress-strain curves were linear to failure, and comparable to standard carbon fiber tension tests.

The strain-to-failure was significantly lower compared to previous reported IM7/PEI samples [4]. This may be due to incompatible surface treatment for the unsized IM7 to the Elium resin. It is difficult to conduct fiber-matrix adhesion testing on 3mm fibers. Interface optimization will be carried out using the unsized IM7 in our future studies as described in [8]. Nevertheless, the key objective was to demonstrate property retention after recycling and both strength and stiffness were the same within their statistical variation. Effects of additional recycling iterations on mechanical properties are planned.

4. CONCLUSIONS

This paper demonstrates recycling of carbon composites made from Arkema Elium resin and IM7 carbon fiber. A low-temperature pyrolysis process was used to remove the polymer content and did not show significant degradation of the fiber length. The *TuFF* short fiber alignment process was used to process the recycled carbon fiber and showed full mechanical property

retention. The closed-loop process recycles the composite, reclaims the fiber content, aligns the fibers using the *TuFF* process and produces new composite components with equivalent mechanical properties. The method reduces material and part cost and allows true recycling and reuse of carbon fiber components into high-performance parts. Future work will optimize the surface treatment before and after recycling to ensure good fiber-resin adhesion and full property translation of the composite.

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6. ACKNOWLEDGEMENTS

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