# Recycling of Carbon Fiber Reinforced Polymers in Subcritical Water with Acetic Acid Amendment

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## Abstract

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A novel single-stage solvolysis process is proposed for recycling carbon fibers from an unknown epoxy-based composite material using 50 wt % acetic acid under subcritical conditions. The process yields 100 % recovery efficiency for fibers in less than 30 min when operating at 300 °C. Qualitative analysis of the fibers using SEM and EDS analysis reveals that the recovered fibers are completely free of epoxy, and the fiber surface does not show any damage. SEM images and gravimetric measurements of the composite at lower temperatures and low residence times also reveal an initial swelling of the CFRP samples, suggesting a two-step process, i.e., the initial swelling of the composite matrix followed by chemical decomposition of the polymer. FTIR and GC-MS analyses confirm epoxy decomposition and formation of aromatic compounds, phenolic derivatives, and high molecular weight compounds.

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## LIST OF ABBREVIATIONS

**ATR-FTIR** - attenuated total reflection Fourier transform infrared

**°C** - Celsius

**CF** - carbon fiber

**CFRP** - carbon fiber reinforced polymer

**DAQ** - data acquisition

**DCM** - dichloromethane

**DGEBA** - diglycidyl ether of bisphenol A

**DI** - deionized

**EDS** - energy dispersive X-ray spectroscopy

**EoL** - end-of-life

**FTIR** - Fourier transform infrared

**GC-MS** - gas chromatography – mass spectrometry

**$H_2O_2$** - hydrogen peroxide

**IPA** - isopropyl alcohol

**M** - molar

**mL** - milliliter

**mm** - millimeter

**MPa** - mega Pascal

**NMR** - nuclear magnetic resonance

**MT** - metric ton

**PID** - proportional integral derivative

**RCF** - recycled carbon fiber

**SEM** - scanning electron microscope

**SS** - stainless steel

**TOF-MS** - time of flight – mass spectrometry

**UD** - unidirectional

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# DEDICATION

To my parents

## 1. INTRODUCTION

The use of composite materials can be dated back to the Mesopotamian era, where people glued strips of wood at different angles and multiple layers to create plywood. From ancient times, humans have had a fascination for creating better and stronger materials for various uses. Today, many things we see and touch is made up of some or several composite materials. These materials have become an integral part of the manufacturing industry, as they provide similar or better material properties and outweigh their counterparts. Composite materials these days are used in automotive and aerospace industries, sports equipment, and other consumer products.

Carbon fiber reinforced polymer (CFRP) primarily consist of two components: the matrix and the reinforcement. The most widely used reinforcement is carbon fiber which provides strength in the composite. The matrix is generally a resin polymer or epoxy, which binds the carbon fiber reinforcement. The two components are combined in a controlled proportion and process, yielding the desired material properties, i.e., high strength and low weight. CFRPs achieve tensile strength 3 to 5 times greater than stainless steel while being 30 to 50 % lighter.

The type CFRP can be broadly classified into thermoplastic and thermoset composites. Thermoplastic composites are formed by heating the matrix-reinforcement mix, which softens the mixture and then cooling it inside molds where it hardens and takes the shape of the mold. The thermoplastic part can be reheated again to soften the matrix and separate the fibers from the matrix. Thermoset composites can be formed in a similar process; however, once the matrix has solidified, it cannot be melted again to separate the composite constituents. The most commonly used CFRPs are thermoset composites since they are more robust and do not deform or lose their mechanical properties because of heat during their intended application.

CFRPs can also be categorized based on the direction of reinforcement inside the composite matrix. Unidirectional (UD) CFRP is a type of composite where all the fibers in the composite align in a parallel direction. In this type of composite, there are no gaps between the reinforcement fibers and are laid flat during the layup/manufacturing step of the composites. Woven CFRPs are the other type of composite characterized by the direction of reinforcement fibers. The fibers are woven in a pattern, and the tows go over and under the adjacent fiber layer.

This manuscript focuses on recovering the fiber reinforcement, *i.e.*, the strands of carbon fibers from an aerospace-grade thermoset UD CFRP composite matrix using a solvolysis process. Various solvents have been tested to determine the suitable process for recycling the carbon fibers from the composite.

## 2. LITERATURE REVIEW

The use of CFRPs has been increasing rapidly over the years; the amount of CFRP production globally in the year 2020 was estimated to be over 130,000 MT. It is estimated that 30% of the total production is disposed of as waste, including the waste generated during the manufacturing process, constituting the End-of-Life (EoL) for the composites. Therefore, recycling most of the generated waste would significantly benefit both the environmental and economic aspects of the CFRP lifecycle. Recycled fibers can be reintroduced in various industries such as the automotive industry, sports and consumer goods.[1-2]

The current technologies used for recycling the fibers from CFRP composites can be broadly categorized into three groups: mechanical, thermal, and chemical processes. Mechanical processes employ a grinding step to physically break the composite material and produce grain-size particles that can be introduced again in the manufacturing step of CFRP composites. Thermal techniques use high temperatures to vaporize the polymer matrix and leave the fibers as a product that can be recovered. Chemical techniques utilize solvents-water mixtures that can chemically decompose the polymers, leaving the fibers intact for subsequent collection. Thermal and chemical processes are preferred over mechanical techniques due to their ability to recover long strands of fibers.

### 2.1 Mechanical Recycling

This technique reduced the size of the recycled components by grinding or crushing using a slow-speed cutting or milling machine.[3-4] The resulting feedstock is classified as (i) coarse recyclate, which has high fiber content that can be incorporated as reinforcement during the subsequent manufacturing cycle and (ii) fine recyclate with high in resin content that can be used as filler material for the resin matrix in the molding step. While the recovered fibers and resins can be reused, there are several technical challenges in re-manufacturing the composite materials. First, the orientation of the fibers cannot be controlled since the aspect ratio of the recovered fibers are unknown and irregular. The mechanical properties of the components manufactured using mechanically recovered fibers have inferior performance due to reduced fiber length. Material propertied worsen with each cycle.[5] The recovered filler is comparatively more expensive than the virgin filler material (such as calcium carbonate or silica) used in CFRP composites.[4]

### 2.2 Thermal Recycling

These processes involve high temperatures; the CFRP composite is incinerated at temperatures in the range of 450 to 700 °C. Pyrolysis, microwave-assisted or fluidized bed pyrolysis can be used with varying process parameters, such as pressure, temperature, and residence time.[4, 6-7] The resin in the composite matrix is vaporized, leaving clean strands of fiber reinforcement. Hence, this process is suitable only for recovering the fibers. The polymer matrix decomposes into two phases: the gaseous low molecular weight (MW) compounds and the high MW compounds such as oils and chars. The latter can condense onto the fibers when cooled.[7] Therefore, recovering the fiber reinforcement requires additional post-processing steps. Thermal recycling has other challenges, including the formation of pollutants, such as toxic gases and particulate matter, as well as char deposition on the equipment and product. Studies have reported that the recovered fibers with oil/char deposits decrease the performance of the recycled CFRP composite.[6-7] High MW hydrocarbons can be broken down into lower MW species via secondary pyrolysis at the higher temperatures[8-9] or fully carbonized,[10] exposing the composite matrix to elevated temperatures can damage the fibers, therefore reducing the mechanical properties of the recycled CFRP composite.[11-13]

## 2.3 Chemical Recycling

In solvolysis, the polymer matrix is disintegrated by dissolving the composite material in a chemical solution, such as acids, bases, alcohols, and other solvents. Generally, water is used as a solvent at hot temperature high-pressure (HTHP) conditions. CFRP recycling has been investigated in subcritical or supercritical water (SCW). Subcritical water (< 374°C) has been studied as a medium for the decomposition of organic compounds,[14-15] and the addition of amendment was also shown to have a positive effect on recalcitrant chemicals like polyfluoroalkyls (PFAS).[16] As the temperature of the SCW ($T > 374°C$, $P > 22.1$ MPa ) can be raised, the decomposition rates of organic compounds are significantly faster than in subcritical water hydrolysis.[14, 17] Addition of an oxidant ($O_2$ or $H_2O_2$) to the system with hydrocarbons results in heat release and offers a convenient way to heat the reactor internally[18-19]. SCWO converts wastes to $CO_2$, $H_2O$, $N_2$, salts, acids, and metal oxides, without producing $NO_x$, $SO_2$, or airborne particulate matter. Fuel-rich SCWO conditions result in partial oxidation and produce high carbon yields[20] that can deposit on reactor wall or recovered fibers.

Chemical recycling can be used for a wide size range of composite materials. Once all the resin matrix is decomposed, the RCFs are collected and cleaned before reuse.[21-22] The fibers retain their original shape and tensile strength.[23-24] This method provides the highest resin decomposition rate amongst the current recycling techniques.[25] One drawback of chemical recycling is the required use of harsh chemicals, such as acids, and requirements for post-processing treatment of effluent.

## 2.4 Current Chemical Recycling Processes

Several laboratory-scale chemical recycling systems have shown near 100 % recovery of CFs under various conditions; different solute and solvent combinations, varying residence times and temperature versus pressure variations have been investigated. In this section, prior works closely related to our approach are presented.

### 2.4.1 CFRP waste recycling using peracetic acid

Das et al. subjected CFRP coupons (30 mm x 25 mm x 2 mm) in a mixture of 14 M glacial acetic acid, 9 M $H_2O_2$, and water at varying concentrations.[26] The vessel was then placed in a hot oil bath (at atmospheric pressure) and allowed to cool naturally to room temperature at the end of the experiment. The presence of $H_2O_2$ in the solvent mixture leads to the *in-situ* formation of peracetic acid, which facilitated the recycling process. The RCFs were cleaned, and the tensile strength was compared to the virgin CFs. The highest resin decomposition ratio reported was at 98.8%. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) were utilized to analyze CF surface conditions; the liquid products were analyzed using Fourier transform infrared (FTIR), Time of Flight – Mass Spectrometry (TOF-MS), Gas Chromatography – Mass spectrometry (GC-MS), Nuclear Magnetic Resonance (NMR), and Pyro-GC/MS. Table 1 summarizes the experimental matrix conditions. They also recovered the acetic acid from the spent liquid products.

**Table 1.** Process parameters for CFRP recycling using peracetic acid

| Solution | Vol. % Acetic Acid | Vol. % $H_2O_2$ | Temperature (°C) | % resin decomposition | Residence time (h) |
|---|---|---|---|---|---|
| Ac100 | 100 | - | 65 | 25.6 | >10 |
| Ac95H5 | 95 | 10 | 65 | 97.2 | 4 |
| Ac90H10 | 90 | 5 | 65 | 98.3 | 4 |
| Ac80H20 | 80 | 20 | 65 | 98.8 | 4 |
| Ac50H50 | 50 | 50 | 65 | 96.5 | 5 |
| Ac20H80 | 20 | 80 | 65 | 98.2 | 5 |
| H100 | - | 100 | 65 | - | - |
| Ac95H5 | 95 | 5 | 28 | 98.3 | 84 |
| Ac95H5 | 95 | 5 | 80 | 98 | 4 |
| Ac95H5 | 95 | 5 | 65 | 67.3 | 8 |
| Ac95H5 | 95 | 5 | 65 | 94.4 | 8 |

### 2.4.2 Near 100% CFRP recycling using ethylene glycol

Yu et al. proposed recycling epoxy-based CFRP using ethylene glycol (EG) for resin decomposition.[27] The EoL CFRP components were immersed in EG and heated up to 160 °C to 180 °C to activate the bond exchange reactions (BER) within the covalent adaptable network (CAN) present in the resin matrix. This enabled the removal of epoxy from the composite, and the fibers were cleaned using secondary steps. The authors also reported that by heating the recovered liquid (containing EG and decomposed epoxy) further, it was possible to evaporate all the residual alcohol solvents. The re-polymerization properties of the thermoset material remained the same as that of the fresh polymers. This process recovered 100% of the constituents in the composite matrix, including the epoxy/polymer resin and the CFs. The recycled fibers retained 95% of the original fibers' tensile strength, and the process did not damage the CFs or the epoxy during recycling. However, epoxy degradation using EG can be challenging due to its operating parameters and system conditions. If the EG present in the system evaporates or insufficient EG can lead to re-polymerization of the decomposed epoxy at high temperatures.

### 2.4.3 Recycling CFRP composite in oxygen in supercritical water

Supercritical water as a medium for CFRP recycling has been recently investigated. Bai et al. reported the recycling of CFs from an epoxy-based composite in oxygen in supercritical water.[28] The system with waste CFRP was heated to 440±10 °C at 30 MPa, with residence times varying from 25 to 35 min. The solid products were cleaned with acetone in a secondary step before surface characterization of the recovered CFs. The RCFs were clean, and the resin decomposition rate was greater than 96%. However, they also reported that the liquid phase contained more than 100% of the expected product; the RCFs surface degradation was confirmed by RCFs surface analysis. The recovered fibers' tensile strength was the same as the original fibers when the resin decomposition was 94-97%. While the SCW may offer fast matrix decomposition rates, the complexity of the system and energy requirement may not be practical for real-world applications.

In this project, we propose a technique to recover 100 % carbon fibers from an unknown CFRP composite material that can be reused for practical applications. Along with this, we have also attempted to identify the intermediary steps involved in the recycling stages of a typical CFRP composite material. A novel feature of this process being the ability to decompose the resin in the composite matrix faster than the processes that have been reported thus far.

## 3. EXPERIMENTAL DESIGN AND METHODOLOGY

### 3.1 Reactor Design

The experiments were carried out in a batch system, comprising a reactor vessel, furnace for heating, and a thermocouple to monitor the internal reactor temperature. The reactor vessel is made out of a Stainless Steel 316 (SS316, **Error! Reference source not found.**) tube from High-Pressure Equipment Inc, (Erie, PA, US). The reactor is 304.8 mm in length with 25.4 mm diameter and had an internal volume of 50 mL. The electrical tubular furnace from Barnstead Thermolyne Corporation (Dubuque, IA, US)., Type F21100 had an internal PID controller to control the temperature. The sections of the furnace open to the atmosphere were sealed using fiberglass insulation. A K-type thermocouple was placed inside the reactor section to monitor the temperature and ensure isothermal reaction conditions during the experiments. Data acquisition module (Omega, TC-08, Stamford, CT, US) was used to read the signal from the thermocouple and translated it pictorially on the laptop using PicoLog 6 thermocouple logger. The schematic of the system is shown in Figure 1. Refer to **Error! Reference source not found.** for a photograph of the batch reactor setup.

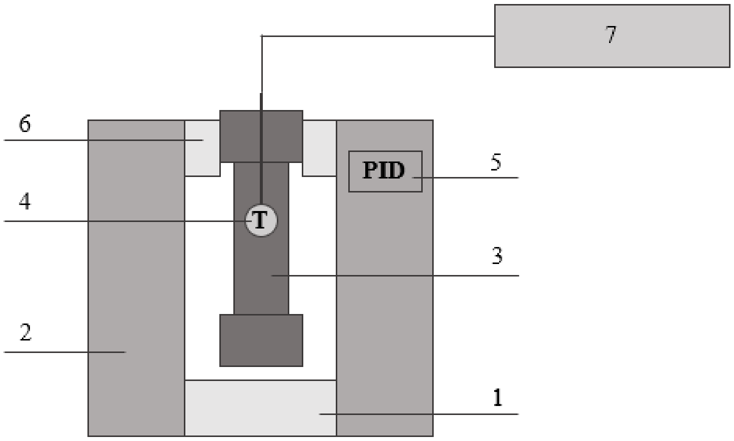


**Figure 1.** Schematic of a batch reactor system used for CFRP recycling consisting of (1) and (6) insulation, (2) electric tubular furnace, (3) reactor vessel (4) internal thermocouple, (5) internal PID controller, and (7) DAQ

### 3.2 Materials and Methodology

Thermoset CFRP composite with unknown composition, type of fiber reinforcement, and CF wt % was used. Several solvent combinations were tested initially (including water, different concentrations of sodium hydroxide, acetic acid, isopropyl alcohol, and ethanol); acetic acid has shown the most promising results and was further investigated. An aqueous solution of 50 wt. % glacial acetic acid (99. %, Fischer Scientific) and 50 % DI water (resistivity 18.2 MΩ-cm) is used for a parametric study. The composite was cut into coupons 50 mm x 10 mm x 2 mm. In the experiment, 35 mL of solvent liquid and 5 g CFRP coupon are loaded into the batch reactor and sealed. The reactor is then placed inside the tube furnace and heated to a target temperature, as shown in Table 2. The datum for each experiment is assigned when the set temperature inside the reactor is reached. Expansion of gases during heating results in an autogenic pressure rise to 10 MPa, keeping all reagents in a compressed liquid phase. The after the target exposure time is reached, the reactor is cooled rapidly by emersion in cold water until it reaches room temperature. **Error! Reference source not found.** shows the temperature profile inside the reactor during a typical experiment. The reactor content is then filtered using a Grade 1 Whatman filter paper (Millipore Sigma, Burlington, MA, US). The liquid consisting of solvent and decomposed resin is stored in a Nalgene vial for further analysis, and the RCFs are rinsed with DI water. The RCFs are further cleaned in an ultrasonic bath for 15 min. in IPA (99.9 %, Sigma Aldrich) to complete the removal of resins of the recovered fibers. The cleaned fibers are then dried in a desiccant dehumidifier for 24 hr. before imaging.

The resin removal rate ($R_R$) for the composite matrix was calculated based on the mass of CFs recovered at the end of each experiment as shown below:

$$R_R = \frac{W_{CFRP} - W_s}{W_{CFRP}} \times 100$$

where, $W_{CFRP}$ is the mass of CFRP composite before the start of the experiment, $W_s$ is the mass of the RCFs collected after the drying.

The chemical composition of the liquid samples was analyzed using ATR-FTIR (ThermoFisher Scientific, Nicolet iS 10 FTIR Spectrometer) and GC-MS (Agilent Technologies, MS: 5973; GC: 6890 with 7683 autosampler). The liquid samples were preprocessed before analyzing in the GC-MS. An aliquot of 5 mL was mixed with 5 mL of dichloromethane (DCM) to extract the organic solvents present in the sample. Sodium hydroxide (ACS reagent, ≥99.0%, anhydrous, granular, Sigma Aldrich) was added to the extracted liquid to remove the water from the organic extracts. The organic compounds in the solution were identified by comparing the mass spectra with the inbuilt NIST database of the instrument.

**Table 2:** Experimental conditions evaluated in this work

| Temperature (°C) | Solvent | Process Amendment | | Residence Time (min.) |
|---|---|---|---|---|
| | | Solution | Concentration (50 wt %) | |
| 200 | DI $H_2O$ | Acetic Acid | 50 | 0, 30, 60, 90, 120 |
| 225 | DI $H_2O$ | Acetic Acid | 50 | 0, 30, 60, 90, 120 |
| 250 | DI $H_2O$ | Acetic Acid | 50 | 0, 30, 60, 90, 120 |
| 275 | DI $H_2O$ | Acetic Acid | 50 | 0, 30, 60, 90, 120 |
| 300 | DI $H_2O$ | Acetic Acid | 50 | 0, 30, 60, 90, 120 |

## 4. RESULTS

Several solvents were screened: NaOH (concentrations: 0.1 M, 0.5 M and 1 M), 10% IPA, 10 wt % ethanol and acetic acid (concentrations in wt %: 10 %, 40 % and 60 %) at 300 °C for 60 min. The liquid products from all the experiments showed some decomposition of the resin; however, the fiber imaging showed that in most cases, the resin was not removed from the composite. The experiment with acetic acid at 40 wt % and 60 wt % showed the best resin removal. Figure 2 shows the liquid and solid products after the end of the experiments for different solvents. The change in color of the liquid is due to the presence of organic compounds from epoxy degradation at an operating condition of 300 °C for 60 min. The composite retained the original shape, i.e., there was no significant change in the samples' physical structure.

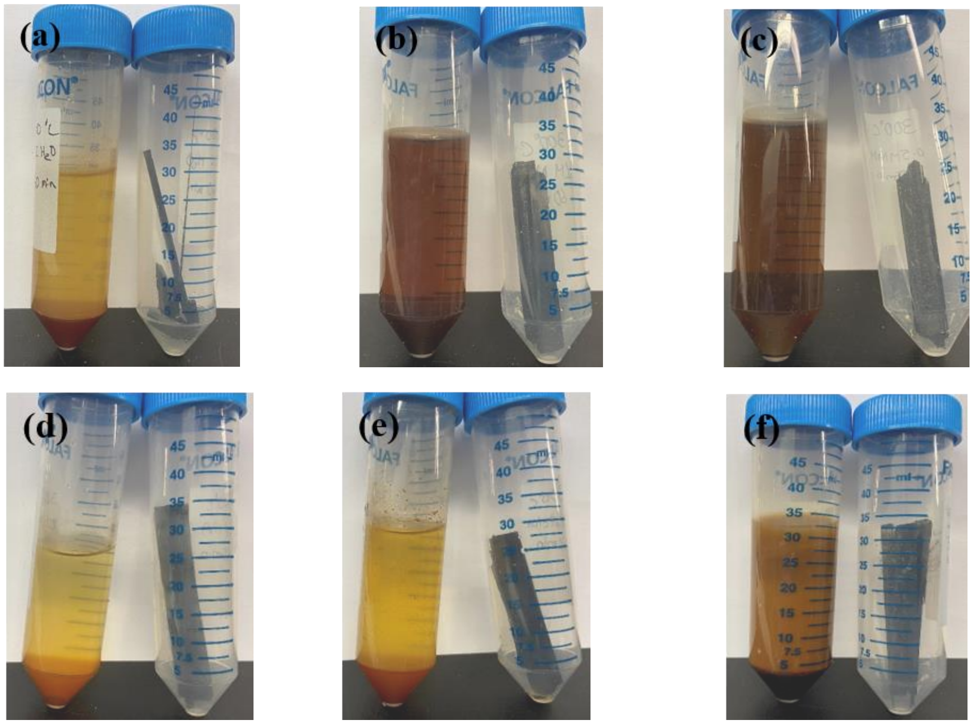


**Figure 2.** Experimental products separated in vials after solvolysis at 300 °C for 60 min. residence time: (a) DI water, (b) 1M NaOH, (c) 0.5M NaOH, (d) 10 wt % IPA, (e) 10 wt % ethanol, and (f) 10 wt % acetic acid

In the parametric study of CFRP treatment, the samples were subjected to an aqueous solution of 50 % acetic acid with varying temperature and residence time. The total fraction of resin in the composite matrix was determined by thermogravimetric analysis (TGA, TA Instruments, Q50), and it was found to be in the range of 26 to 32 % of the total mass of the original CFRP. After each experiment, the products were collected in two vials for solvent and fibers each. The liquid containing decomposed resin was analyzed using ATR-FTIR and GC-MS. Note that the formation of a thick viscous layer was observed around the rim of the vial when the liquid was left unattended for more than 24 hr. The recovered RCFs (Figure 3) were analyzed using SEM and EDS to check for the resin residue on the fiber surface.

**Figure 3.** Clean fibers recovered after recycling the composite matrix at 300 °C and 30 min. with 50 % acetic acid

### 4.1 Analysis of liquid containing decomposed resin

The solvents from each of the experiments were analyzed using ATR-FTIR to determine the composition of the solvent after the experiments. Figure 4 shows the IR spectra of solvents recovered after 200 °C and 300 °C at 30 min residence time. The spectral peaks at 1390 $cm^{-1}$ and 1703 $cm^{-1}$ in the IR region indicate the presence of phenolic, carbonyl, and aliphatic ketones.[29-32] The missing absorption peak of C-N bonds at 1110 $cm^{-1}$ suggests the decomposition of polymers initiate due to cleavage of these bonds. Furthermore, the C–OH group at 1050 cm$^{-1}$ is oxidized to form a C=O bond at 1703 cm$^{-1}$. The absorption peaks for aromatic rings at 1580 – 1615 cm$^{-1}$ are low due to the thermal and chemical degradation of these compounds at tested conditions. Peaks corresponding to alkyl aryl ethers, amines, aliphatic nitro compounds, and O–H stretching can be observed at 1265 cm$^{-1}$, 1640 cm$^{-1}$, 1370 cm$^{-1}$ and 3400 cm$^{-1,}$ respectively. The formation of similar functional groups has been previously attributed to the degradation of DGEBA epoxies,[26, 32] that are generally used in aerospace grade applications.

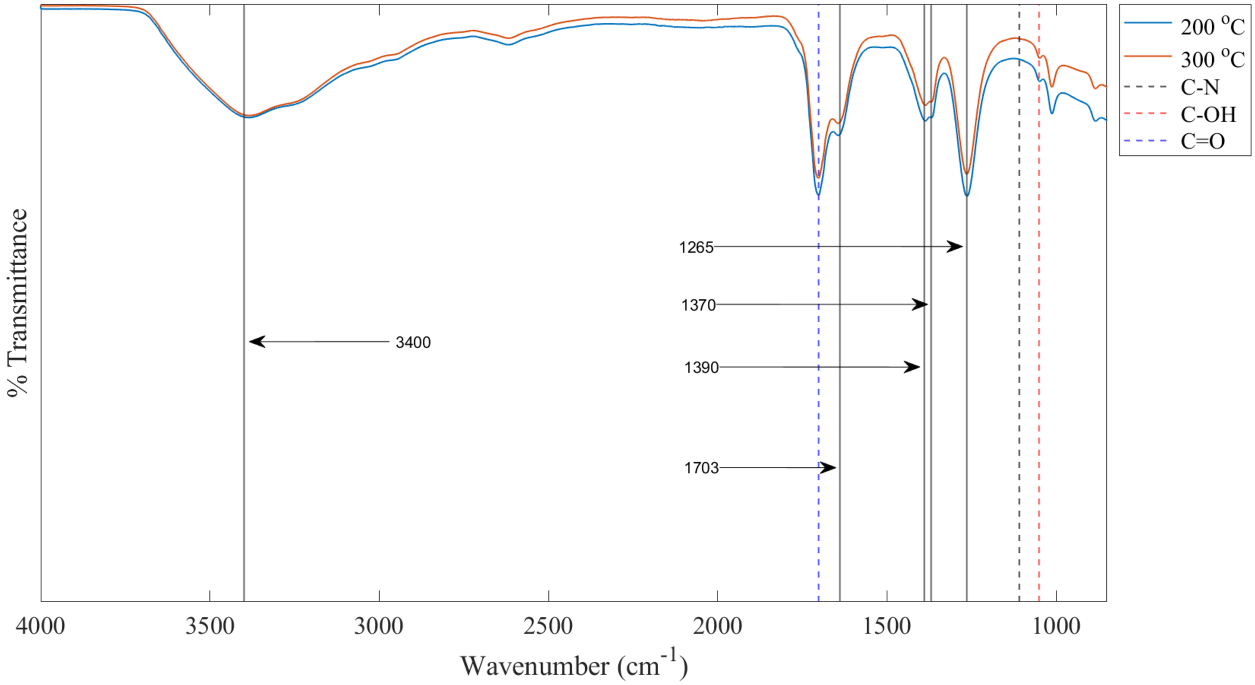


**Figure 4.** FTIR analysis of recovered decomposed epoxy matrix at 200 °C and 300 °C

The GC-MS data of the recovered liquid provides additional insight into the degradation of compounds during the recycling process. **Error! Reference source not found.** shows the GC-MS spectra of the liquid recovered after 300 °C and 30 min residence time. The presence of aromatic rings and phenolic derivatives indicates that the starting composite was a diglycidyl ether of bisphenol A (DGEBA) based epoxy.[33-34] The GC-MS was also able to detect the presence of high molecular weight compounds, which also explains the sedimentation that was seen around the vials containing the recycled epoxy solvent, see **Error! Reference source not found.**.

### 4.2 Analysis of recovered fibers

The recovered fibers were dried and weighed to check for resin decomposed during each experiment. Note that the time reported in the table is the period of exposure to solvent once the target reactor temperature is reached. The time to reach that temperature varies depending on the conditions, this delay is reported in Table 3. The temperature profile during a typical experiment is shown in Figure A3.

**Table 3:** Resin removal rate (%) with 50 % acetic acid for various conditions, positive numbers = mass decrease

| Temp. (°C) | Time to reach target T (min.) | Percent weight removal ( % ) | | | | |
|---|---|---|---|---|---|---|
| | | 0 min | 30 min | 60 min | 90 min | 120 min |
| 200 | 85 | 0 | -3.96 | -3.61 | -4.40 | -5.99 |
| 225 | 80 | -4.35 | -4.49 | -6.53 | -18.6 | -3.92 |
| 250 | 80 | -6.82 | -3.39 | -2.04 | -16.52 | 3.98 |
| 275 | 80 | -6.00 | 1.01 | 15.81 | 20.92 | 25.71 |
| 300 | 80 | 2.08 | 28.49 | 31.92 | 32.97 | 31.71 |

Figure 5 shows the resin decomposition trends for all conditions of the experimental matrix. Here, it is interesting to observe that for all residence times at 200 °C and 225 °C, the overall weight of the RCF coupon increases indicating that the solvent penetrates the resin matrix before the depolymerization reaction occurs. Previous studies have reported that swelling can be used as a pretreatment process in the recycling of CFRPs.[35-36] Figure 5 shows that, in all cases, before the composite mass is reduced, the mass weight increases by as much as 20 %. In the 200°C cases, the weight continues to increase (~7%) after 120 min of exposure to solvent. The at 225°C and 250°C the maximum swelling is observed at 90 min (after the target temperature is reached), the associated weight gain is ~ 16-19%, which is 50-75% of the volume fraction of resin contained in the sample (determined by TGA analysis). The 275 °C and 300 °C cases do not have upward likely to swelling occurring during the heating procedure before t=0 min is reached. However, the 275 °C sample at t=0 min has greater mass than the original coupon. At 275 °C (120 min.) and 300 °C (30 to 120 min.), we were able to recover long and clean fibers, with epoxy completely removed, see Figure 3. From the latter case with higher temperatures, the swelling step appears to be a shorter process than the epoxy decomposition process. However, additional investigation is needed to determine the rates for these steps. Here, adjusting for the time required to heat the system is a challenge.

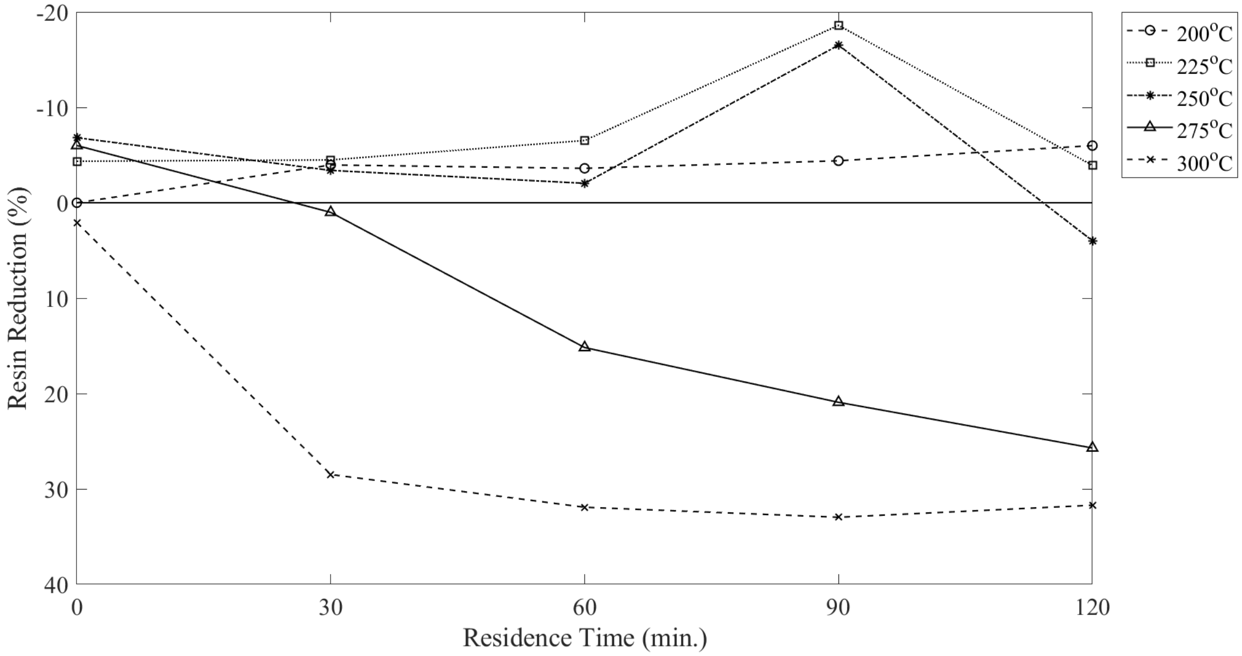


**Figure 5.** Resin reduction percentage of the recovered CFs for various conditions

Note that polymer swelling was not observed when other amendments were used under similar conditions. We hypothesize that swelling plays a crucial step in matrix breakdown during the recycling of CFs from the composite matrix.

SEM images of the composite and fibers before (Figure 6) and after the recycling process shows 100 % removal of the epoxy in the composite matrix using 50 % acetic acid (Figure 7). EDS analysis (Figure 8) of the surface of RCFs confirms 100 % resin decomposition and carbon as its only constituent present as the end product.

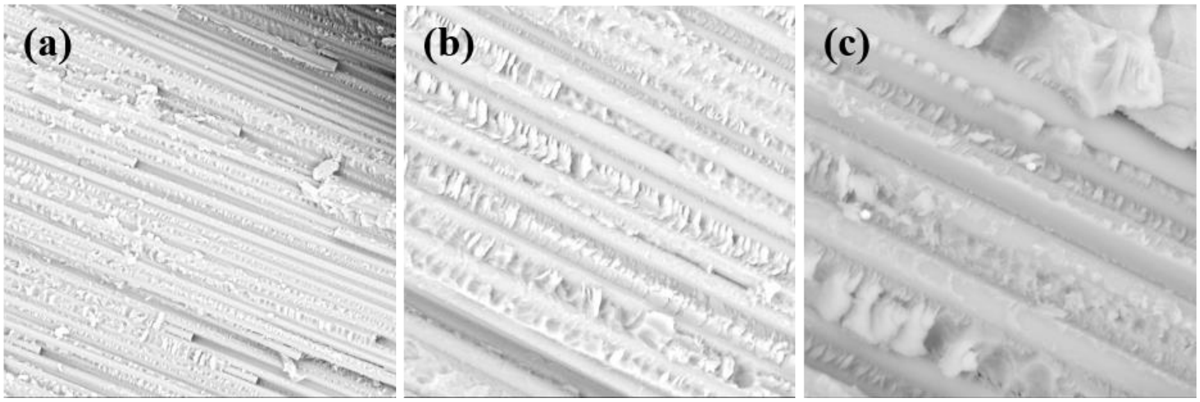


**Figure 6.** SEM images of CFRP composite before recycling (magnification: 850,2250,4000x)

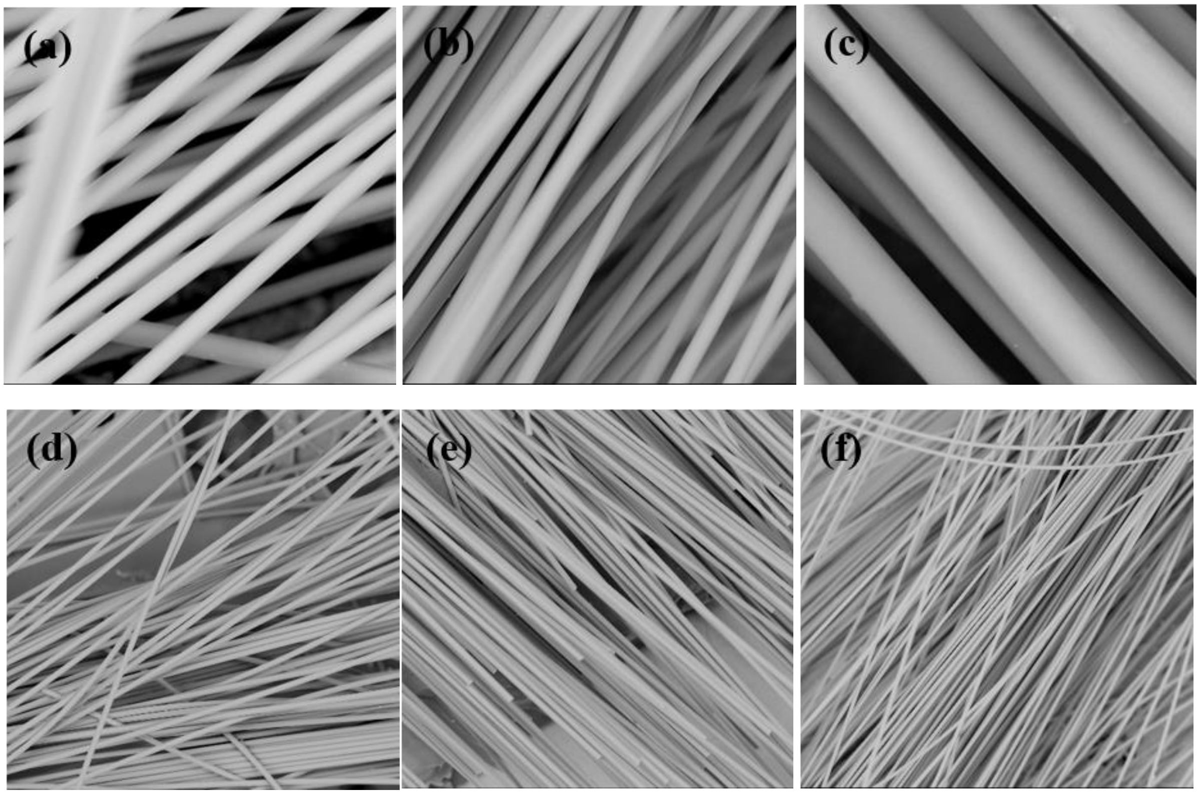
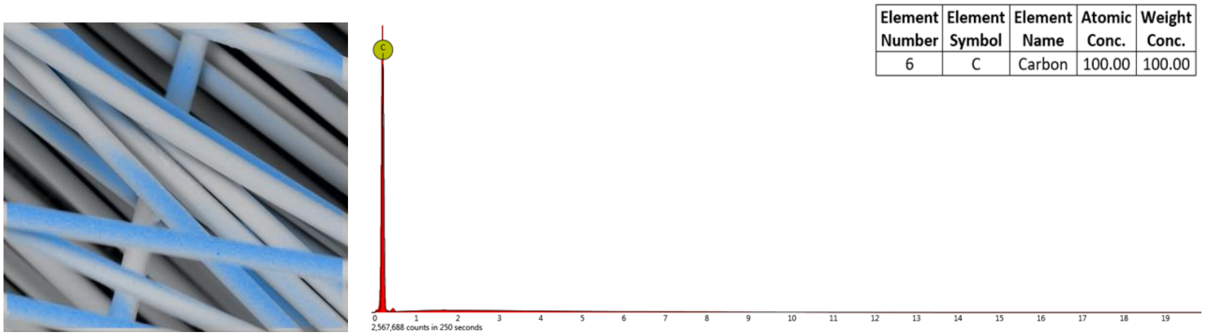


**Figure 7.** SEM images of recovered fibers at 300 °C: (a), (b), (c) strands of clean fibers showing 100 % resin removal (magnification: 2500x) and (d), (e) and (f) multiple layers of clean fibers (magnification: 590x)



| Element Number | Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|---|---|---|---|---|
| 6 | C | Carbon | 100.00 | 100.00 |

**Figure 8.** EDS analysis of the recovered fibers treated at 300 °C for 30 min.

## 5. CONCLUSION

This project demonstrates the recycling of aerospace-grade CFRP composite material in hot compressed water with 50 % acetic acid under subcritical conditions. A lab-scale system has been developed in used in the study for recycling of CFs.  Decomposition of DGEBA based epoxy matrix is reported as a function of time and reactor temperature. Subcritical acetic acid treatment facilitated epoxy swelling and was followed by chemical decomposition. The approach facilitates a two-step recycling process, including swelling of polymers and recovery, into a single stage. In this work, we show 100 % resin decomposition of the epoxy at 275 °C (120 min.) and 300 °C (residence times ~ 30 min.) which is the fastest CF recovery process reported from a CFRP matrix. This process can be scaled up, it could recover long carbon fibers and with simple distillation techniques. It is possible to recover acetic acid from the liquid, thus making the entire process further efficient and greener.

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# APPENDIX A

**Figure A1.** SS316 reactor vessel for recycling CFRP composite

**Figure A2.** Lab-scale batch reactor system including furnace, reactor and DAQ

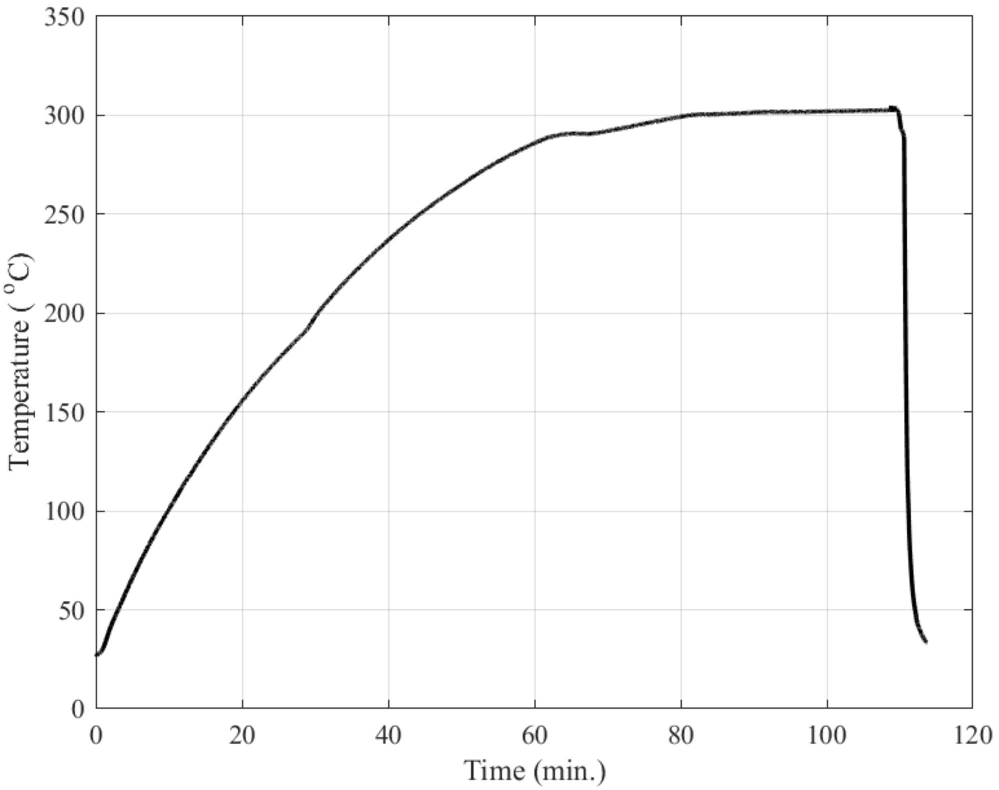

**Figure A3.** A plot of heating and cooling of the reactor for an experiment run at 300 °C with a residence time of 30 min.

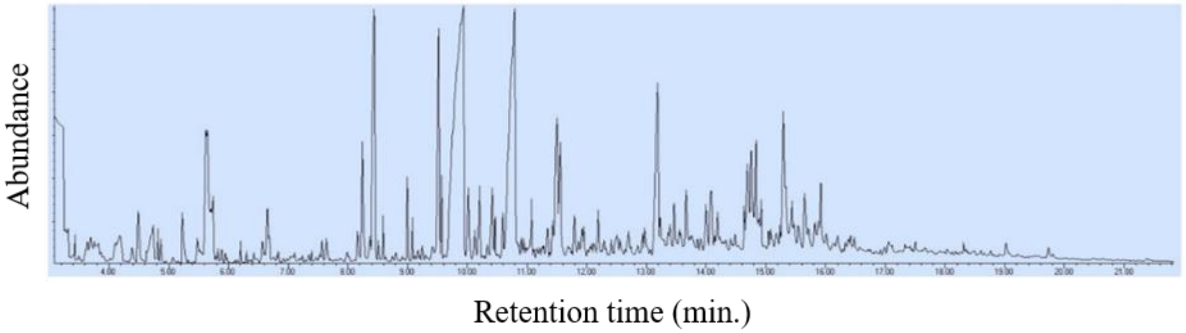

**Figure A4.** GCMS plot of recovered liquid after treating the sample at 300 °C for 30 min.

**Figure A5.** Sedimentation of high molecular weight compounds on the filter paper after decomposing the epoxy matrix

**Error! Reference source not found.** (a) and (b) are SEM images of fibers undergoing swelling, where the solvent penetration into the composite layers can be seen. Condition with maximum swelling is displayed in Figure 8 (c), this indicates the decomposition of an epoxy matrix into a high molecular weight compound, hence, the viscous nature of the epoxy and appearance of a coalesced composite matrix.

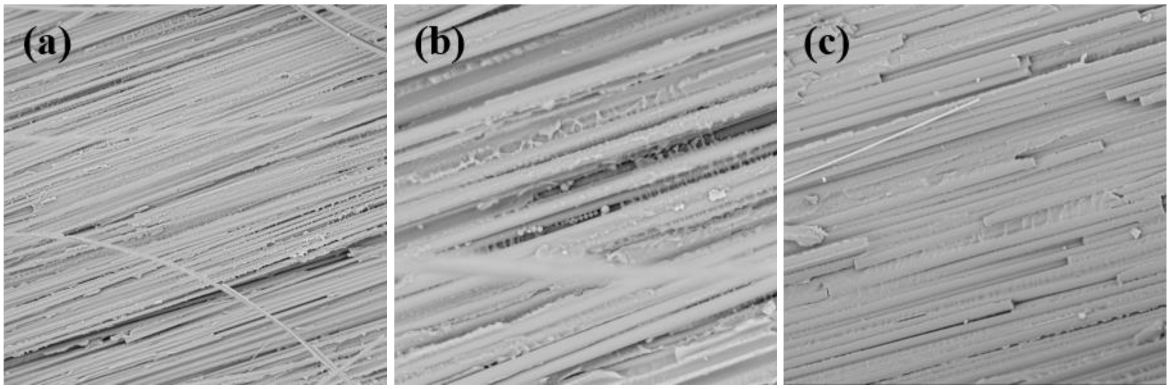

**Figure A6:** SEM images of recovered fibers along with the composite during swelling: (a), (b) at 250 °C and 30 min., and (c) 250 °C and 90 min.