

## OPTIMISATION OF SOLVOLYSIS FOR RECYCLING CARBON FIBRE REINFORCED COMPOSITES

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### Abstract

Solvolysis processes have been used to degrade the resin of two different varieties of epoxy based carbon fibre reinforced composite (CFRC) materials. A degradation of up to 98% has been achieved when processing material at a temperature of 320 °C using a supercritical solvent mixture of acetone and water. Increasing the processing time from 1 to 2 hours shows an increase in the degradation of only 10% and there does not appear to be any benefit in processing the material beyond this time. Due to the batch conditions used, it is necessary to rinse the fibres with acetone after processing to remove remaining organic residue. Washing the fibres at supercritical batch conditions, however, does not efficiently remove the residue compared to a simple hand washing with acetone. Shredding the sample prior to processing also does not have a significant effect. The process investigated requires 19 MJ.kg<sup>-1</sup> of fibres recovered and, since the process has not yet been optimised, shows strong potential for future development especially since it allows for the recovery and reuse of organic resinous products.

### 1 Introduction

With the ever increasing use of carbon fibre reinforced composites (CFRCs), there is growing concern regarding the level of waste the industry is expected to produce. Approximations vary, but some estimates state the demand for CFRCs will increase by up to 10% per year from 78,000 t in 2014 to 150,000 t in 2020 [1, 2]. In addition to various products reaching end of life (EoL), there is also the necessity to dispose of the waste generated from the manufacturing process, which makes up as much as 40% of all material needing reprocessing [3]. Despite currently being a relatively cheap disposal method at £82.60 per tonne in the UK [4], landfilling waste is the least preferred option: it poses an environmental hazard, reflects poor resource management due to the high financial and energy cost of manufacturing (up to £40 kg<sup>-1</sup> and 600 MJ.kg<sup>-1</sup> of fibre) [5] and is already outlawed in Germany with other countries expected to follow suit [6].

Current commercialised recycling technologies for CFRCs focus on the use of pyrolysis but do not effectively close the loop of the supply chain due to the loss of the polymer matrix which is typically about 50 wt.% of the material. For this reason, solvolysis has started to gain more attention. At low temperature and pressure (LTP), catalysts and acidic or alkaline solutions must be used to achieve complete degradation [7-11] however; the resulting solutions are often a significant hazard with respect to health, safety and the environment. At near- or supercritical conditions, even the hardest, most stable thermoset (e.g. epoxies) and thermoplastic (e.g. PEEK) resins can be fully degraded using solvents such as water, methanol, ethanol, propanol and acetone without the need for additional

catalysts [12-15]. The effect of using water in conjunction with organic solvents has also been studied to identify an optimum combination which allows for maximum degradation at a lower temperature and pressure [7]. Oliveux, et al. [7] have since shown that using 80 vol.% acetone with 20 vol.% water and a resin concentration of approximately 30 mg.mL<sup>-1</sup> allows for maximum degradation of a model epoxy resin. This work aims to deepen the understanding of the process in order to improve its efficiency and optimise parameters such as treatment time and material loading rate while maintaining the fibre quality and producing valuable organic products from resin degradation.

## 2 Materials and Methods

### 2.1 Materials

Two different material types were examined. Type 1 consisted of plates of composite material made of RTM6 epoxy resin and 20 plies of T700 6k carbon fibre woven fabric. These were cut into pieces measuring (50 x 50) mm<sup>2</sup> to (50 x 80) mm<sup>2</sup>. The thickness of the plates was 6 ± 1 mm and fibre volume content was 53 ± 1%.

Type 2 was an end of life sample of an Airbus A320 provided both shredded and unshredded to examine how the resin degradation is influenced by the form of the original material.

Analytical research (AR) grade acetone was purchased from Sigma Aldrich and used to make a solvent mixture of 80 vol.% acetone and 20 vol.% water for all experiments.

### 2.2 Fibre Recovery

All experiments were completed in an electrically heated, 5 L hastelloy batch reactor purchased from Parr Instrument Company. The mass of the samples was determined through using a concentration of organic material in the range of 51 to 59 g.L<sup>-1</sup> of solvent assuming 100% degradation. All samples were placed into a stainless steel basket to avoid contact with the reactor walls and therefore pyrolysis of the material. The heating phase required approximately 75 min to reach 320 ± 5 °C inducing a pressure of 170 ± 10 bar. The system was maintained at this temperature for 1 to 2 hours before removing the heat supply. Due to the weight of the reactor, it was not possible to lift it from the oven to cool; therefore, the cooling phase required about 2 h for the temperature to decrease to below 200 °C and a further 18 h to reach 35 °C. After this time, the reactor was opened and the fibres and liquid fraction containing dissolved organic products from the resin degradation were recovered. The fibres were then washed either by hand with pure acetone or in three post-solvolytic steps at the same conditions to remove remaining residue on the fibre surface as shown in Table 1.

**Table 1.** Variation in experimental conditions

Exp. No.	Material	Reaction Time (h)	Washing conditions
1	Type 1 – RTM6	1	None
2		2	None
3		2	Hand wash
4		2	3 washes at 320 °C, 170 bar
5	Type 2 – A320 unshredded	2	None
6		2	Hand wash
7	Type 2 – A320 shredded	2	Hand wash

## 2.3 Fibre Characterisation

The fibres were analysed by Environmental Scanning Electron Microscopy (ESEM) using a Philips XL30 FEG ESEM. Samples were cut and mounted on to adhesive stub mounts. Although carbon fibres are conductive, the samples were coated in platinum to improve image quality using an EMSCOPE SC500 low-vacuum sputter coater. Once mounted and coated on the stubs, the samples were loaded individually into the ESEM and the sample chamber was evacuated. The images were taken at varying magnification levels at an acceleration voltage of 20 kV.

The organic residue remaining on the recovered fibre bundles was measured using calcination. Approximately 1.5 g samples were placed into five crucibles and heated to 500 °C in air. The samples were removed at regular intervals and weighed. When the reduction in mass was negligible, all remaining residue was considered to be completely removed. The weight percentage of the organic material remaining after processing was then calculated using equation (1) and the resin removal yield quantified with equation (2).

$$R_f\% = \frac{m_i - m_f}{m_i} \quad (1)$$

$$Y\% = \frac{R_i - R_f}{R_i} \quad (2)$$

Where: Y = Resin removal yield

$R_i$  = Initial resin content

$R_f$  = Resin content after processing

$m_i$  = Mass of sample after processing (g)

$m_f$  = Mass of sample after calcination (g)

An average yield could then be taken from the five samples. The initial resin content of the shredded and unshredded Type 2 material was found in a similar manner using equation (1) and used to calculate the percentage of resin removed in experiments 5 to 7 (Table 1).

## 2.4 Assessment of Energy Efficiency

The energy demand of the process was calculated by monitoring the current drawn by the reactor using a Fluke 345 PQ Clamp Meter. A value for the current was taken every 5 s and used in equation (3) to calculate the power as the reactor relies on a single phase, rather than 3-phase supply [8]. Assuming this is constant over each 5 s period, the energy can then also be calculated. The total energy used throughout the process was then determined by summing each value.

$$P = I V \quad (3)$$

Where: P = Power (W)

I = Current (A)

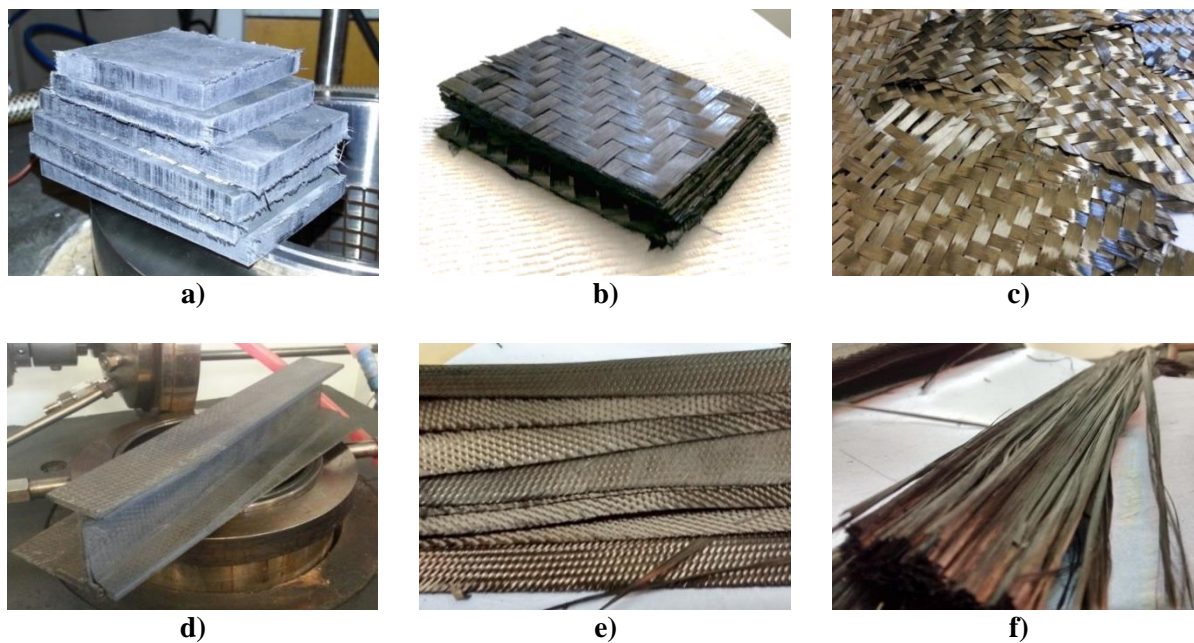
V = Voltage (V)

A standard UK mains voltage of 240 V was used to power the reactor.

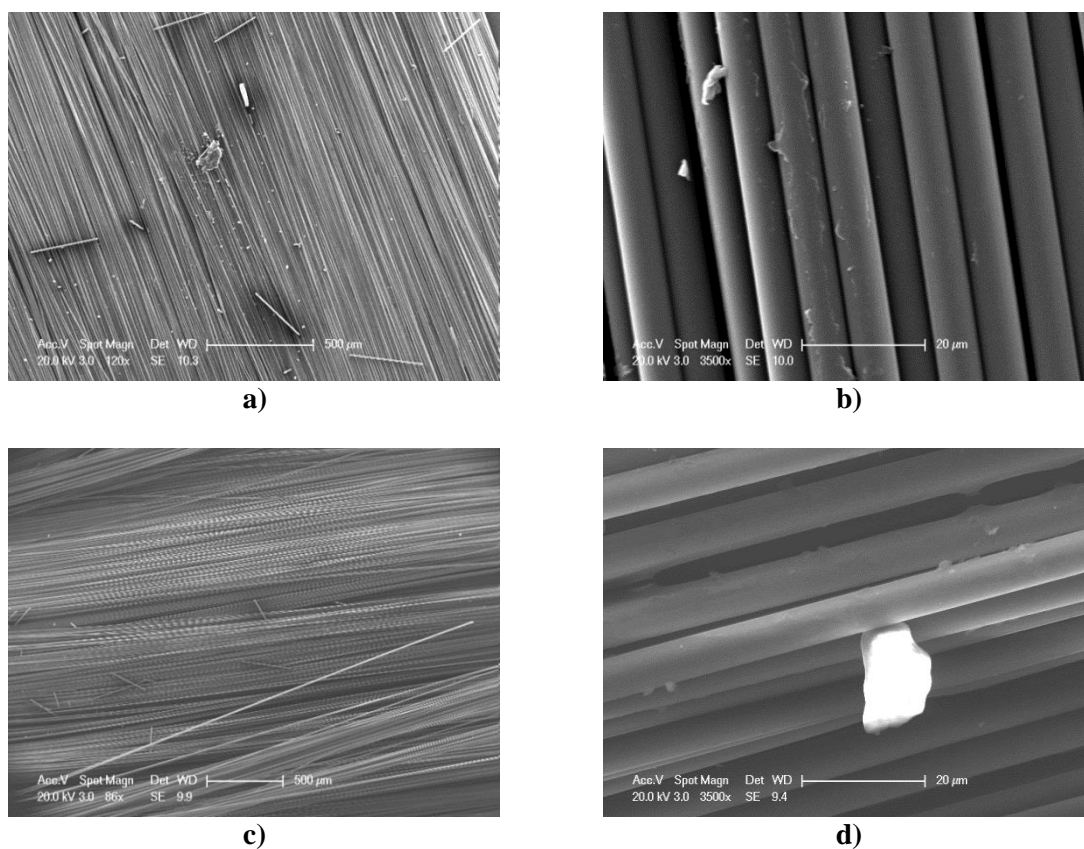
## 3 Results and Discussion

### 3.1 Fibre Characterisation

Solvolysis of both material types enabled the recovery of fabric pieces which were perfectly separated from resin and from each other, in addition to retaining their woven architecture as illustrated by Figure 1. Some fibres were also imaged by ESEM (see Figure 2) and showed a very clean surface with



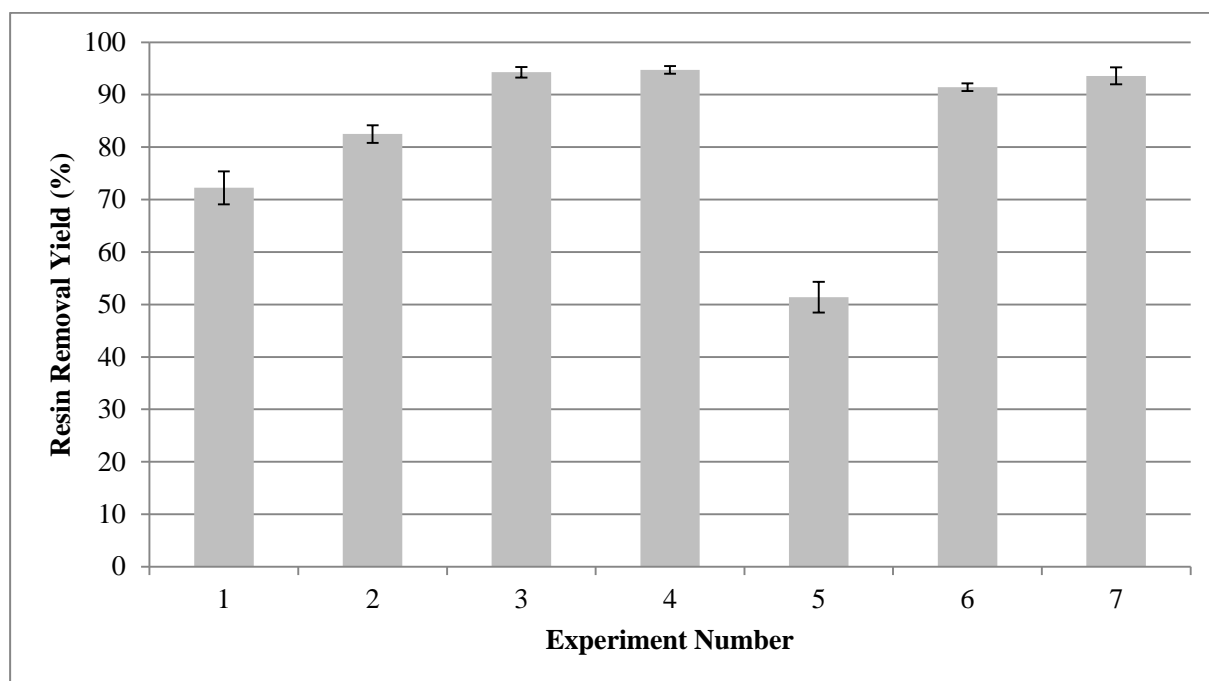
**Figure 1.** Samples of a) Type 1 RTM6 composite materials before solvolysis; b) and c) Fibre pieces recovered from Type 1 material after solvolysis; d) Type 2 A320 unshredded composite material before solvolysis; e) and f) Fibre pieces recovered from Type 2 material after solvolysis



**Figure 2.** ESEM images of: a) and b) unwashed carbon fibres recovered after solvolysis; c) and d) carbon fibres after slight wash with acetone

only a small amount of organic residue coating the fibres. Some resin dust was observed and could mostly be removed thanks to a light washing with acetone.

The mass of resin remaining after solvolysis was quantified through calcination, the results of which are shown in Figure 3. As illustrated, the vast majority of resin can be completely degraded and removed after processing the material for 2 hours at 320 °C and 170 bar. A yield of  $72 \pm 3\%$  is achieved after just 1 hour at these conditions, however, it is necessary to continue processing materials for a further hour to achieve an additional 10% in degradation. Although samples from Experiment 1 and 2 were not washed with acetone, this difference indicates not all organic molecules had been degraded and were still adhered to the fibre surface.



**Figure 3.** Degradation of resin achieved under different conditions

As shown by experiments 2, 3, 5, 6 and 7 (Table 2), rinsing the recovered fibres by hand with acetone removes the majority of the organic products from the surface of the fibres indicating the substance remaining on the surface is no longer a resin but organic products re-adhered during the cooling phase. This is most noticeable in experiments 5 and 6 where the resin removal yield increased by 40% from  $51 \pm 3\%$  in the former to  $91 \pm 1\%$  after washing by hand. In addition, it was observed that for both materials, the outside layers were noticeably stiffer than those on the inside before washing. Hand washing and supercritical washing led to similar resin removal yields (Figure 3); therefore, reprocessing the fibres using the same supercritical conditions is not the most efficient way to wash the fibres. However, it shows that by renewing the solvent during solvolysis would avoid the degradation products re-adhering to the fibres. This is also demonstrated by the use of Soxhlet extraction which gave a value for resin removal yield of 3 wt.% and 1 wt.% for unwashed and washed fibres respectively. At the boiling temperature of acetone, it was not possible to remove the entire residue even after 6 cycles. This method therefore enabled the removal of resin dusts not stuck to the fibre surface but not the residue coating the surface. In turn, this could mean the residue is adhered to the surface and may not hinder good adhesion with a new resin. A semi-continuous solvolysis process, however, in which the solvent is renewed continuously, could enable a total removal of organic residue.

Although Oliveux, et al. [7] observed that a resin concentration of 30 g.L<sup>-1</sup> allows for a higher degradation of a model epoxy resin, the results presented suggest that nearly doubling the concentration up to approximately 60 g.L<sup>-1</sup> does not reduce the process efficiency. This has important consequences in terms of process optimisation; by increasing the mass of material within the reactor, the cost and energy consumption per kg of recovered fibre will be greatly reduced.

### 3.2 Energy Consumption

During the heating phase, a constant power of approximately 450 W was drawn by the reactor. Upon reaching 320 °C, this then fluctuated between 50 W and 400 W in order to maintain the temperature, resulting in total energy consumption over the 85 minute heating phase and 2 hour reaction phase of about  $3.69 \pm 0.01$  MJ. With the reactor loading at 300 g of material, the specific energy requirement was therefore  $19.2 \pm 0.1$  MJ.kg<sup>-1</sup> of fibre recovered. Relative to the energy demand to manufacture virgin fibres of 198 to 594 MJ.kg<sup>-1</sup> [6], this represents a significant energy saving of 90 to 96% and is approximately 40% less than estimates for the energy consumption during pyrolysis [9]. It is also important to note this energy consumption is for an unoptimised process. Operating semi-continuously should allow a lower temperature and higher reactor loading to be used, resulting in a significantly lower energy demand as reported in [10]. Solvolysis also prevents the generation of pollutants such as CO<sub>2</sub> which are released to the atmosphere during pyrolysis and allows the recovery of valuable organic molecules thereby closing the loop of the supply chain. For these reasons, it is likely the environmental impact of solvolysis across other impact categories (global warming potential, ozone depletion potential, eco-toxicity, etc.) is also lower than other recycling technologies. However, there will be an energy cost associated with the recovery of the solvent and the organics and so a complete life cycle assessment will need to be conducted in order to quantify the total environmental impact.

## 4 Conclusion

Implementing a mixture of acetone and water as a solvent, it was possible to achieve complete resin degradation when the temperature is maintained at 320 °C for 2 hours. However, due to the batch conditions used, it is necessary to thoroughly wash the fibres with acetone to fully remove any remaining organic molecules adhered to the surface. This is essential for the recovery of clean fibres suitable for reuse in the manufacture of a new composite material in addition to retaining a mixture of valuable organic compounds. By experimenting with two material types, these preliminary results suggest the developed process is suitable for a range of feedstocks. In order to enhance the resin removal, reduce process time and minimise the energy requirement, future work will focus on operating semi-continuously with the aim of determining optimum operating parameters.

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### References

- [1] T. Kraus and M. Kuhnel, "Composites Market Report 2014," Federation of Reinforced Plastics, Berlin, 2014.
- [2] Reinforced Plastics, "Global carbon fibre market remains on upward trend," Elsevier Ltd., 2014.
- [3] S. J. Pickering, "Recycling technologies for thermoset composite materials - current status.," *Composites Part A*, vol. 37, pp. 1206-15, 2006.
- [4] HM Revenue & Customs, "Excise Notice LFT1: a general guide to Landfill Tax," 2015. [Online]. Available: <https://www.gov.uk/government/publications/excise-notice-lft1-a-general-guide-to-landfill-tax/excise-notice-lft1-a-general-guide-to-landfill-tax#rates-of-tax>. [Accessed 13 11 2015].

- [5] [W. Carberry, "Aerospace's role in the development of the recycled carbon fibre supply chain.," in \*Carbon Fibre Recycling and Reuse 2009 Conference\*, Hamburg, Germany, 2009.](#)
- [6] [G. Oliveux, L. O. Dandy and G. A. Leeke, "Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties," \*Progress in Materials Science\*, vol. 72, pp. 61-99, 2015.](#)
- [7] [G. Oliveux, L. O. Dandy and G. A. Leeke, "Degradation of a model epoxy resin by solvolysis routes," vol. 118, pp. 96-103, 2015.](#)
- [8] G. G. Karady and K. E. Holbert, *Electrical Energy Conversion and Transport*, 2nd ed., New Jersey: IEEE Press, 2013.
- [9] [R. A. Witik, T. R., V. Michaud, C. Ludwig and J. -. A. E. Manson, "Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling," \*Composites: Part A\*, vol. 49, pp. 89-99, 2013.](#)
- [10] [R. Pinero-Hernanz, J. Garcia-Serna, C. Dodds, J. Hyde, M. Poliakoff, M. J. Cocero, S. Kingman, S. Pickering and E. Lester, "Chemical recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions," \*The Journal of Supercritical Fluids\*, vol. 46, pp. 83-92, 2008.](#)
- [11] [W. Dang, M. Kubouchi, S. Yamamoto, S. Sembokuya and K. Tsuda, "An approach to chemical recycling of epoxy resin cured with amine using nitric acid.," \*Polymer\*, vol. 43, pp. 2953-8, 2002.](#)
- [12] [Y. Liu, L. Meng, Y. Huang and J. Du, "Recycling of carbon/epoxy composites," \*Journal of Applied Polymer Science\*, vol. 94, no. 5, pp. 1912-6, 2004.](#)
- [13] [S. H. Lee, H. O. K. J. S. Choi, C. K. Lee, Y. K. Kim and C. S. Ju, "Circulating flow reactor for recycling of carbon fiber from carbon fiber reinforced epoxy composite," \*The Korean Journal of Chemical Engineering\*, vol. 28, no. 2, pp. 449-54, 2011.](#)
- [14] [P. Yang, Q. Zhou, X. X. Yuan, J. M. N. van Kasteren and J. Z. Wang, "Highly efficient solvolysis of epoxy resin using poly\(ethylene glycol\)/NaOH systems.," \*Polymer Degradation and Stability\*, vol. 97, pp. 1101-6, 2012.](#)
- [15] [J. R. Hyde, E. Lester, S. Kingman, S. Pickering and K. H. Wong, "Supercritical propanol, a possible route to composite carbon fibre recovery: a viability study.," \*Composites Part A\*, vol. 37, pp. 2171-5, 2006.](#)
- [16] [C. Fromonteil, P. Bardelle and F. Cansell, "Hydrolysis and oxidation of an epoxy resin in sub- and supercritical water," \*Industrial Engineering and Chemistry Research\*, vol. 39, pp. 922-5, 2000.](#)
- [17] [I. Okajima, K. Yamada, T. Sugeta and T. Sako, "Decomposition of epoxy resin and recycling of CFRP with sub- and supercritical water," \*Kagaku Kogaku Ronbunshu\*, vol. 28, pp. 553-8, 2002.](#)
- [18] [J. Li, P. L. Xu, Y. K. Zhu, J. P. Ding, X. L. Xue and Y. Wang, "A promising strategy for chemical recycling of carbon fiber/thermoset composites: self accelerating decomposition in a mild oxidative system.," \*Green Chemistry\*, vol. 14, pp. 3260-3, 2012.](#)