RECYCLING CARBON FIBRE WITH AN ACETONE/WATER SOLVENT AND ZINC CHLORIDE CATALYST: RESIN DEGRADATION AND FIBRE CHARACTERISATION

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ABSTRACT

The degradation of a carbon fibre reinforced epoxy resin with an acetone/water mixture and $ZnCl_2$ catalyst was investigated. The solvent/catalyst system achieved a resin removal yield in excess of 94% after 1.5 h at 290°C and 45 min at 300°C. Single fibre tensile testing indicated an increase in fibre strength after the recycling process. The strongest fibres were recovered using a reaction temperature of 290°C and exhibited a strength of 3.21 ± 1.10 GPa. The technique developed therefore appears to recover high quality fibres while reducing the temperature by 30°C and process time by 25% when compared to earlier work.

1. INTRODUCTION

The current and expected growth within the manufacturing and use of carbon fibre reinforced composites (CFRCs) has been well described [1-3], however, this growth is driving a need for improved recycling techniques. Although pyrolysis processes are able to recover fibres with similar mechanical properties to virgin material [4, 5], the polymer matrix is incinerated resulting in the loss of up to 50 wt.% of the composite and generating significant quantities of emissions. Solvolytic technologies have the potential to also recover organic compounds from the matrix, thereby potentially improving resource efficiency and reducing environmental impact. Under low temperature and pressure (LTP, < 200°C, ~ 1 bar) conditions, strong acids, alkalis and/or oxidising agents are necessary to fully decompose the resin. Use of these substances, however, results in particularly hazardous organic liquid products which are difficult to reuse or dispose of [1, 6-9].

Alternatively, generally recognised as safe (GRAS) solvents such as short chain alcohols and acetone can be used at near- or supercritical conditions, either alone or mixed with water, to degrade thermoset polymer matrices [10-17]. Use of alkaline and weak Lewis acid catalysts have also been shown to be effective under these conditions [9], with more recent research suggesting that the presence of chloride ions can accelerate the degradation reaction [18]. It is possible to recover fibres with similar mechanical properties to virgin material after processing at temperatures in the range of 300 to 400°C [13, 14], however, the effect of chloride ions on fibre quality has not been previously studied. This work aims to determine the effect of combining a weak Lewis acid with an acetone/water mixture on the degradation of a commercial CFRC and to assess the influence of the process conditions on virgin fibres.

2. EXPERIMENTATION

2.1 Materials

The degradation reaction was investigated using samples of CFRC measuring (10 x 10 x 6) ±1 mm^3 with a fibre volume content of 53 ± 1%. This consisted of 20 plies of woven Toray T700 6k carbon fibre and an RTM6 epoxy resin. As one of the hardest polymers to degrade, if the developed process is able to recover fibres from this material, it should be applicable to a wide range of CFRCs. The resin content was calculated to be 36 wt.% using densities of carbon fibre and epoxy resin of 1.80 and 1.14 kg.m^{-3} respectively [19, 20]. This value was confirmed using thermogravimetric analysis (TGA) with an Exstar 6000 supplied by Seiko Instruments Inc.

The effect of the recycling conditions on the fibre quality was assessed using virgin Toray T700 carbon fibre. The fibres had been sized, but not used to make a composite material.

Analytical research (AR) grade acetone and zinc chloride ($ZnCl_2$) were supplied by Sigma Aldrich. Acetone was mixed with water from the mains supply in a ratio of 80:20 v/v before adding $ZnCl_2$ to make solutions with a concentration of 0.05 and 0.10 M.

2.2 Fibre Recovery

All experiments were realised with an electrically heated, 100 mL tubular batch reactor provided by Parr Instruments Inc. 4.17 ± 0.02 g of the CFRC and a 120 ± 10 mm length of the virgin fibre were placed into a stainless steel basket before loading into the reactor with 50 mL of the solvent /catalyst system. This equated to a resin concentration of 30 ± 1 mg$_{resin}$. mL$_{solvent}^{-1}$. The process consisted of heating, reaction and cooling phases; the times taken for each are shown in Table 1, along with the process conditions investigated with the 0.05 M $ZnCl_2$ solution.

Target Temperature (± 2°C)	Induced pressure (± 2 bar)	Time (± 1 min)		
		Heating phase	Reaction phase	Cooling phase
270	105	26		25
280	120	28	0, 10, 20, 30, 60, 90, 120, 150	25
290	140	30		27
300	160	32	0, 10, 20, 30, 45, 60	28

Table 1. Process conditions investigated with the 0.05 M $ZnCl_2$ solution and associated heating, reaction and cooling times.

2.3 Fibre Characterisation

2.3.1 *Resin Removal Yield (RRY)*

To determine the resin removal yield (RRY) of the CFRC, two independent methods were used. In Method 1, samples were weighed before and after processing and it was assumed that the difference in mass was equivalent to the mass of resin removed by the recycling process. The RRY was then calculated with Equation (1). Method 2 involved calcining the recovered fibres at 500°C in air using a muffle furnace. Samples were removed from the furnace, cooled

to room temperature and weighed at regular intervals. After between 3 and 20 minutes depending on the sample, the reduction in mass was negligible and it was therefore assumed all remaining organic material had been removed. The resin content after processing (before calcining) was calculated using Equation (2) and the RRY then determined with Equation (3). An average was taken from the RRY given by Method 1 and Method 2 to determine the final value.

$$RRY\ \% = \frac{m_i - m_p}{m_r} \times 100 \tag{1}$$

$$R_f\% = \frac{m_p - m_f}{m_p} \times 100 \tag{2}$$

$$RRY\ \% = \frac{R_i - R_f}{R_i} \times 100 \tag{3}$$

Where: RRY = Resin removal yield (%), m_i = Initial mass of the sample (g), m_p = Mass of the sample after processing (g), m_r = Initial mass of resin present, m_f = Mass of sample after calcination, R_f = Resin content after processing (%)and R_i = Initial resin content (%).

2.3.2 Scanning Electron Microscopy (SEM)

Fibres were recovered after processing for 1 h at 300°C with 0.05 and 0.10 M $ZnCl_2$ catalyst solution and were inspected using SEM with a Philips XL30 FEG ESEM. Samples were mounted onto adhesive stub mounts and coated with platinum using an EMSCOPE SC500 low-vacuum sputter coater. Although carbon fibres are electrically conductive, a metallic coating is able to improve image quality. Samples were loaded individually into the ESEM and images were taken at magnifications in the range of 1,500 to 8,000 with an acceleration voltage of 20 kV.

2.3.3 Single Fibre Tensile Testing (SFTT)

The tensile strength of the recovered fibres was examined through single fibre tensile testing (SFTT) as specified in ISO 11566:1996 [21]. A single fibre was isolated and mounted across a paper frame with a gauge length of 20 mm. Optical microscopy at x40 magnification was used to indicate the frame contained one filament only and to measure the fibre diameter. This was taken to be the same as the manufacturer's data (7 µm) and there was no discernible difference between samples. Each specimen was clamped in the grips of an Instron 5566 tensile testing machine and the sides of the paper frame were cut away leaving the fibre suspended. Tensile tests were conducted with a 10 N load cell and an extension rate of 0.2 mm.min^{-1}. The force-displacement curves were recorded and the failure load was measured with Bluehill software. At least 30 fibres were examined for each of the reactor conditions given in Table 2. The tensile strength was then calculated with Equation (4).

$$\sigma_F = \frac{F_{max}}{A_f} = \frac{4F_{max}}{\pi d_f^2} \tag{4}$$

Where σ_f = Fibre strength (Pa), F_{max} = Maximum recorded load (N), A_f = Fibre cross-sectional area (m^2), and d_f = Fibre diameter (m).

Sample	Reaction Temperature (± 2°C)	Induced Pressure (± 2 bar)	Reaction time (± 1 min)	No. of samples
1	Virgin fibres			35
2	290	140	90	30
3	300	160	45	30

Table 2. Recycling conditions of fibres used in single fibre tensile testing.

3. RESULTS

3.1 Fibre Recovery

The effect of increasing temperature and reaction time on RRY is shown in Figure 1 with the error bars indicating the maximum and minimum values calculated when using Methods 1 and 2. The two values obtained were generally within 5% of each other with the largest variation at 270°C, 150 min where there was a difference in RRY given by the two methods of 10%.
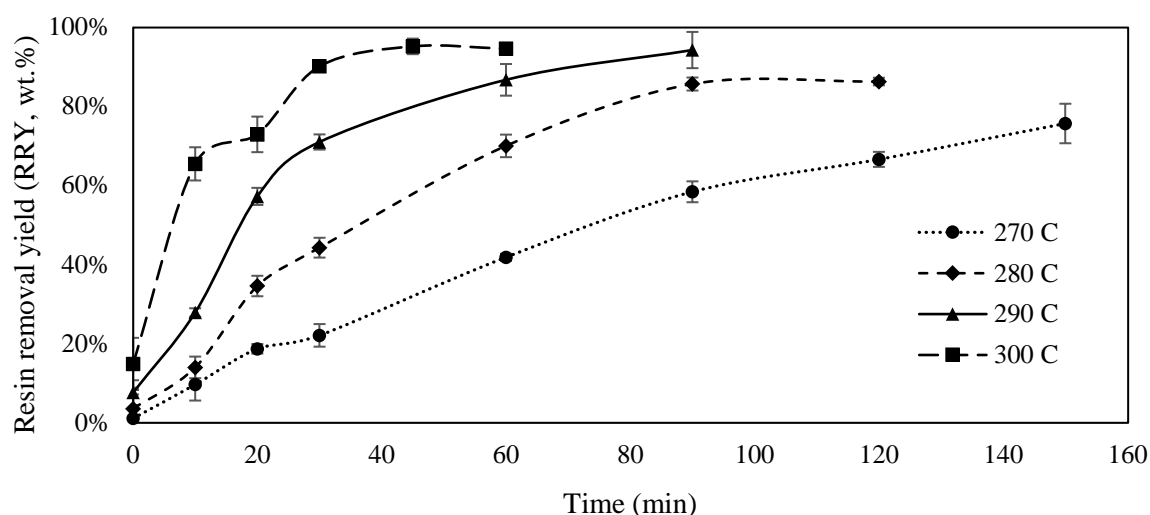

Figure 1. Resin removal yield obtained at various process times and temperatures with a 0.05 M $ZnCl_2$ solution.

At 270 and 280°C, it was not possible to fully strip the resin from the fibre surface in the reaction times investigated; as both of these curves appear to plateau at 75.5% and 86.1% respectively, the results suggest that this temperature must be exceeded in order to fully degrade the resin. Figure 2a also demonstrates that at 280°C, it was not possible to separate the plies into individual tows, however, by raising the temperature to 290°C, clean fibres are recovered, as shown in Figure 2b. With a reaction time of 1.5 h, a RRY of 94.1% is achieved while a similar yield (95.0%) is observed in half the reaction time at 300°C, demonstrating the strong relationship between temperature and degradation rate. This could be due to operating within the supercritical region of the solvent mixture under these conditions. Here, the di-electric constant is dramatically reduced due to the breaking of hydrogen bonds between molecules [17]. This gives rise to a higher diffusivity and lower viscosity which in turn facilitates better mass transfer of organic products, improved solvent efficiency and enhanced reactivity. The critical point is likely to lie between that of acetone (235°C, 48 bar) [22] and water (374°C,

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220 bar) [23], however, it was not possible to find data regarding the critical point of this mixture in the literature. Compared to earlier work [15], the data presented demonstrates that the inclusion of a 0.05 M $ZnCl_2$ catalyst facilitates a reduction in reaction temperature from 320 to 290°C while also reducing process time by 25%. Similar effects of $ZnCl_2$ have previously been reported, however, less severe conditions and longer reaction times were investigated [18].
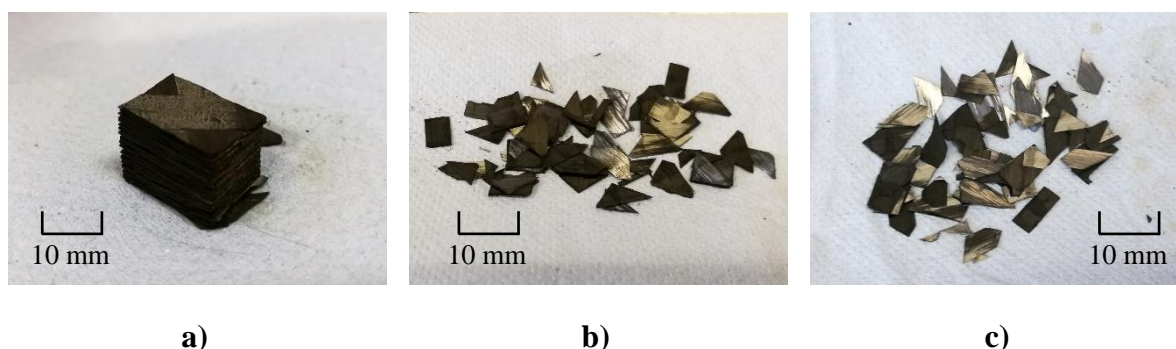

a) **b)** **c)**

Figure 2. Samples of carbon fibre reinforced epoxy resin after processing with a 0.05 M $ZnCl_2$ catalyst and acetone/water solvent at a) 280°C, 2.5 h; b) 290°C, 1.5 h; and c) 300°C, 45 min.

3.2 Scanning Electron Microscopy

Following the degradation process, a light blue sheen was visible on the surface of some fibre tows. Closer inspection with SEM (Figure 3) revealed the presence of small deposits on the fibre surface. This is likely to be a deposit of the catalyst which may affect adhesion to a new resin. When rinsed with water, this deposit was easily removed, thus facilitating the recovery of clean fibres. Furthermore, it was also not possible to identify any surface defects or fractures within the fibres which suggests little damage to the material. However, the current data does not show any change in the surface functional groups. Previous work analysing virgin and recycled material has demonstrated that a reduction in oxygen concentration results in the loss of the interfacial shear strength of the fibres [24]. Therefore, further work is necessary to determine whether this solvent/catalyst system causes a change in the surface chemistry which may in turn influence adhesion to a new resin.

3.3 Single Fibre Tensile Testing

The mechanical integrity of virgin and recovered fibres was investigated through tensile strength measurements, the results of which are displayed in Figure 4. As surface defects act as failure points and are randomly distributed along the fibre length, there is a large range of values recorded as indicated by the error bars. Fibres processed at both 290 and 300°C represent a significantly increased tensile strength compared to virgin fibre of 81.7 and 22.9% respectively. Although this is a relatively large difference between virgin and recycled fibres, increases in strength have previously been noted in earlier work [24, 25]. This is possibly due to the removal of weak graphitic planes (and therefore some surface defects) [6], thereby resulting in an increase in tensile strength.

Raising the process temperature from 290 to 300°C causes a decrease in tensile strength from 3.21 ± 1.10 to 2.25 ± 1.63 GPa. There is also a much larger range of values given by the higher process temperature, indicating a wider variability in fibre quality. For these reasons, the

current data suggest that it is beneficial to minimise the operating temperature although this results in doubling the necessary reaction time to achieve sufficient resin degradation.
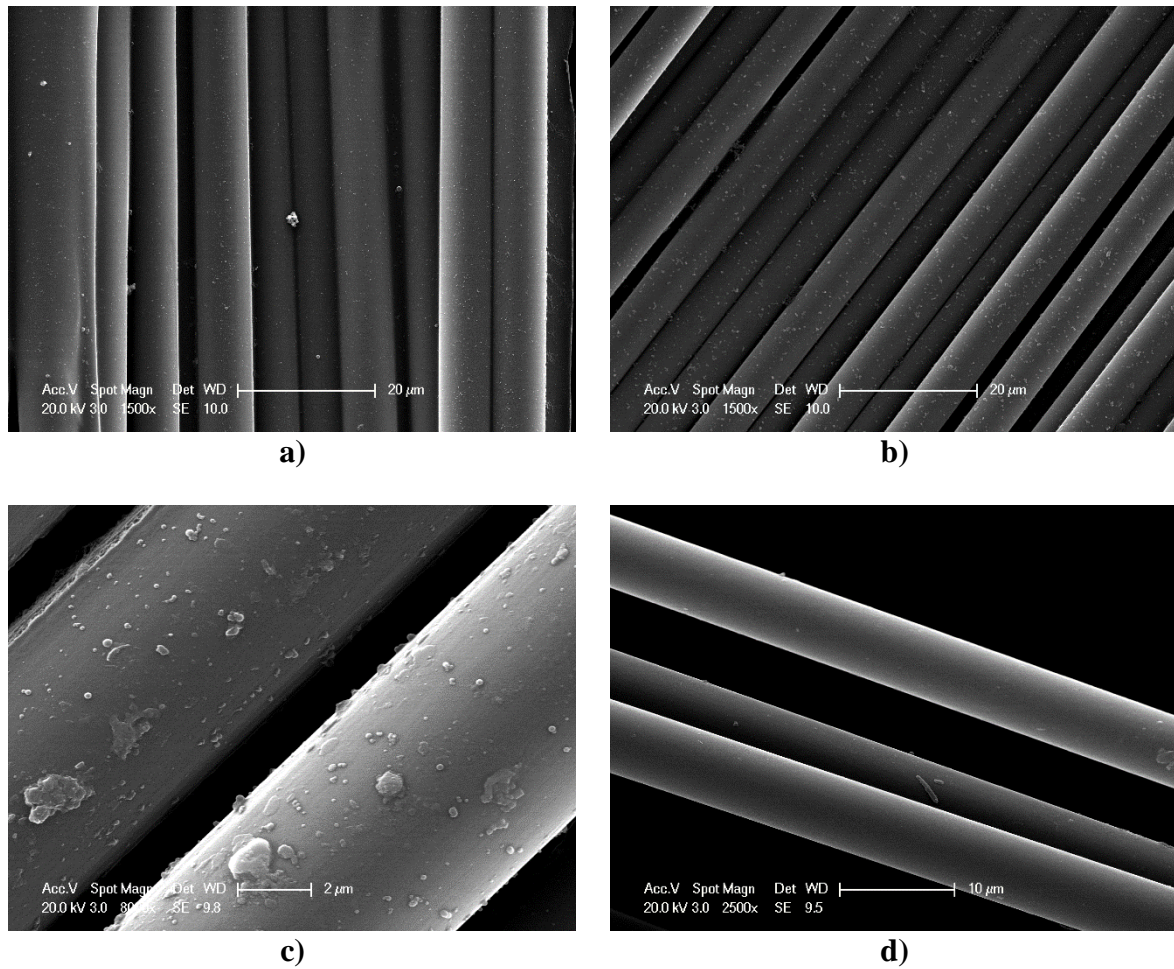

Figure 3. SEM images of fibres recovered after processing with an acetone/water solvent and ZnCl$_2$ catalyst at a concentration of a) 0.05 M; b) and c) 0.10 M and d) 0.10 M with light wash with water.
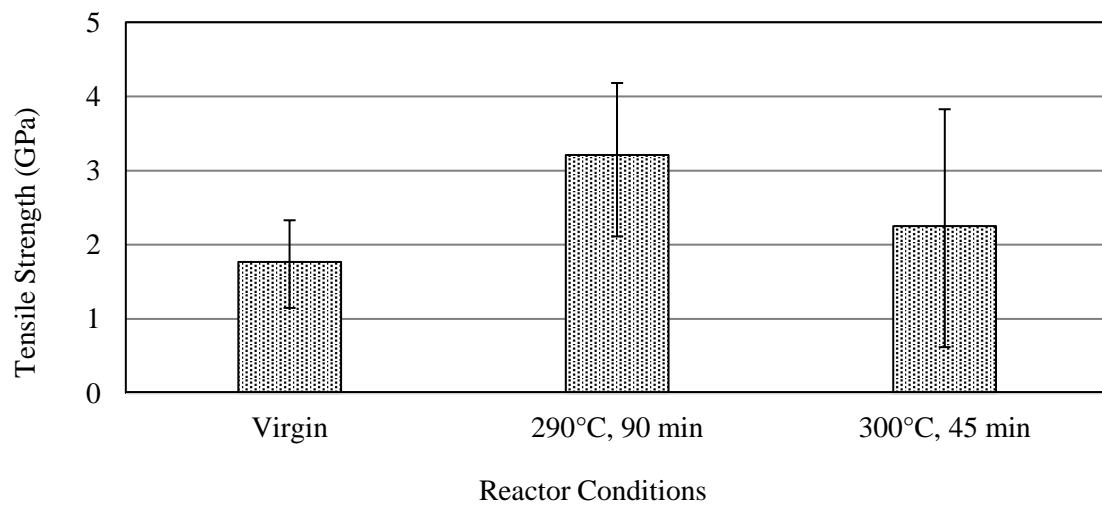

Figure 4. Single fibre tensile tests of carbon fibres recovered after processing at 290°C, 90 min and 300°C, 45 min

4. CONCLUSIONS

The current work demonstrates that a 0.05 M solution of $ZnCl_2$ is able to enhance the degradation of a carbon fibre reinforced epoxy resin using an acetone/water solvent. After processing at 290°C for 1.5 h or 300°C for 45 min, it was possible to recover strong, clean fibres with a RRY in excess of 94%. The research presented therefore demonstrates $ZnCl_2$ is able to reduce process temperature and reaction time by 30°C/30 min or 20°C/75 min when compared to previous studies [15]. This represents significant energy, time and financial savings when considering an industrial scale process.

SEM images of fibres recovered after processing at 300°C showed a slight deposit of the catalyst on the fibre surface. Although this may affect adhesion to a new resin, all residue was easily removed with water. There was no indication of any surface fractures, however, SFTT suggests that a lower reaction temperature of 290°C facilitates the recovery of higher strength fibres. Under these conditions, there was an increase in strength of 81.7% when compared to virgin material suggesting that the developed technique is able to recover fibres suitable for reuse in a new composite material.

5. REFERENCES

1. 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.

2. M. Sauer and M. Kuhnel, "Composites Market Report 2017," Carbon Composites, Augsburg, Germany, 2017.

3. Acmite Market Intelligence e.K., "Market Report: Global Carbon Fiber Composite Market," Gurit Holding AG, Ratingen, 2014.

4. S. Pimenta and S. T. Pinho, "Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook," *Waste Management,* vol. 31, no. 2, pp. 378-392, 2011.

5. J. Yang, J. Liu, W. Liu, J. Wang and T. Tang, "Recycling of carbon fibre reinforced epoxy resin composites under various oxygen concentrations in nitrogen–oxygen atmosphere," *Journal of Analytical and Applied Pyrolysis,* vol. 112, pp. 253-261, 2015.

6. T. A. Langston and R. D. Granata, "Influence of nitric acid treatment time on the mechanical and surface properties of high-strength carbon fibres.," *Journal of Composite Materials,* vol. 48, no. 3, pp. 259 - 276, 2014.

7. 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.

8. P. Yang, Q. Zhou, X. Y. Li, K. K. Yang and Y. Z. Wang, "Chemical recycling of fiber-reinforced epoxy resin using a polyethylene glycol/NaOH system," *Journal of Reinforced Plastics and Composites,* vol. 33, no. 22, pp. 2106-14, 2014.

9. Y. Liu, J. Liu, Z. Jiang and T. Tang, "Chemical recycling of carbon fibre reinforced epoxy resin composites in subcritical water: Synergistic effect of phenol and KOH on the decomposition efficiency," *Polymer Degradation and Stability,* vol. 97, no. 1, pp. 214-220, 2012.

10. I. Okajima, M. Hiramatsu, Y. Shimamura, T. Awaya and T. Sako, "Chemical recycling of carbon fiber reinforced plastic using supercritical methanol," *The Journal of Supercritical Fluids,* vol. 91, pp. 68-76, 2014.

11. I. Okajima, K. Watanabe, S. Haramiishi, M. Nakamura, Y. Shimamura and T. Sako, "Recycling of carbon fiber reinforced plastic containing amine-cured epoxy resin using supercritical and subcritical fluids," *The Journal of Supercritical Fluids,* vol. 119, pp. 44-51, 2017.

12. Y. Yang, R. Boom, B. Irion, D.-J. van Heerden, P. Kuiper and H. de Wit, "Recycling of Composite Materials," *Chemical Engineering and Processing: Process Intensification,* vol. 51, pp. 53-68, 2012.

13. H. Yan, C. X. Lu, D. Q. Jing, C. B. Chang, N. X. Liu and X. I. Hou, "Recycling of carbon fibers in epoxy resin composites using supercritical 1-propanol," *New Carbon Materials,* vol. 31, no. 1, pp. 46-54, 2016.

14. J. R. Hyde, E. Lester, S. Kingman, S. Pickering and K. H. Wong, "Supercritical propanol, a possible route to carbon fibre recovery: a viability study.," *Composites Part A,* vol. 37, pp. 2171-5, 2006.

15. M. Keith, G. Oliveux and G. Leeke, "Optimisation of solvolysis for recycling carbon fibre reinforced composites," in *European Conference on Composite Materials 17*, Munich, 2016.

16. G. Oliveux, J. -L. Bailleul, A. Gillet, O. Mantuax and G. A. Leeke, "Recovery and reuse of discontinuous carbon fibres by solvolysis: Realignment and properties of remanufactured materials," *Composites Science and Technology,* vol. 139, pp. 99-108, 2017.

17. L. Henry, A. Schneller, J. Doerfler, W. M. Mueller, C. Aymonier and S. Horn, "Semi-continuous flow recycling method of carbon fibre reinforced thermoset polymers by near- and supercritical solvolysis," *Polymer Degradation and Stability,* vol. 133, pp. 264-74, 2016.

18. T. Liu, M. Zhang, X. Guo, C. Liu, T. Liu, J. Xin and J. Zhang, "Mild chemical recycling of aerospace fiber/epoxy composite wastes and utilization of the decomposed resin," *Polymer Degradation and Stability,* vol. 139, pp. 20-27, 2017.

19. Toray Carbon Fibers America, Inc, "Technical Data Sheet No. CFA-005," Toray Carbon FIbers America, Inc, California, 2016.

20. Easy Composites Ltd., "Technical Data Sheet: Epoxy Infusion Resin," Easy Composites Ltd. , Stoke on Trent, United Kingdom, 2010.

21. International Organisation for Standardisation, "ISO 11566:1996: Carbon fibre - Determination of the tensile properties of single-filament specimens," International Organisation for Standardisation, Geneva, Switzerland, 2011.

22. National Institute of Standards & Technology, "Acetone," U. S. Department of Commerce, 2011. [Online]. Available: https://webbook.nist.gov/cgi/cbook.cgi?ID=C67641&Type=PC. [Accessed 2 May 2018].

23. National Institute of Standards and Technology, "Water," National Institute of Standards and Technology, 2017. [Online]. Available: http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=4. [Accessed 03 April 2017].

24. G. Jiang, S. J. Pickering, E. H. Lester, T. A. Turner, K. H. Wong and N. A. Warrior, "Characterisation of carbon fibres recycled from carbon fibre/epoxy resin composites using supercritical n-propanol," *Composites Science and Technology,* vol. 69, no. 2, pp. 192-198, 2009.

25. D. T. Burn, L. T. Harper, M. Johnson, W. N. A., U. Nagel, L. Yang and J. Thomason, "The usability of recycled carbon fibre in short fibre thermoplastics: interfacial properties," *Journal of Materials Science,* vol. 51, no. 16, pp. 7699 - 7715, 2016.