Parameter optimisation of combined pyrolysis and oxidation for recycling of CFRP composites

Y. Wei and S. A. Hadigheh
School of Civil Engineering, Faculty of Engineering, The University of Sydney, NSW 2006, Australia
yaning.wei@Sydney.edu.au
ali.hadigheh@sydney.edu.au

THE UNIVERSITY OF SYDNEY

ICCM 23
INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS
BELFAST 2023
30 JULY – 4 AUGUST

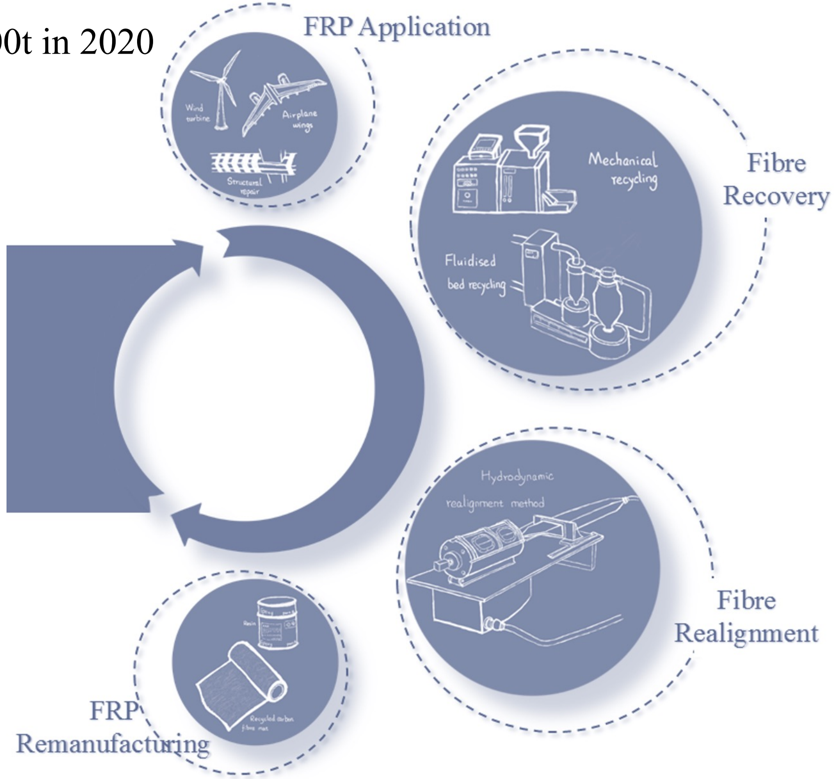
CRICOS 00026A

Table of contents

Research Background

The predicted amount of wasted carbon fibre:
10000t in 2005 --- 57,000t in 2010 --- 88,000t in 2015 --- 130,000t in 2020 --- 263,000t in 2030 [1]

- ❑ Establishing a closed-loop life cycle for CFRP composites is crucial to protect our environment and to maximise material utilisation and energy efficiency.



[1] Witik, R. A., Teuscher, R., Michaud, V., Ludwig, C. and Månson, J.-A. E. (2013). Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling. Composites Part A: Applied Science and Manufacturing, 49, 89-99.

Research Background

environmental protection

- Minimise the amount of CFRP waste sent to landfill
- Reduce non-renewable energy consumption
- Minimise the green house effect

'green engineering'

- expand the material options for 'green engineering' which is defined as building with fewer negative effects on the natural environment, society and human health

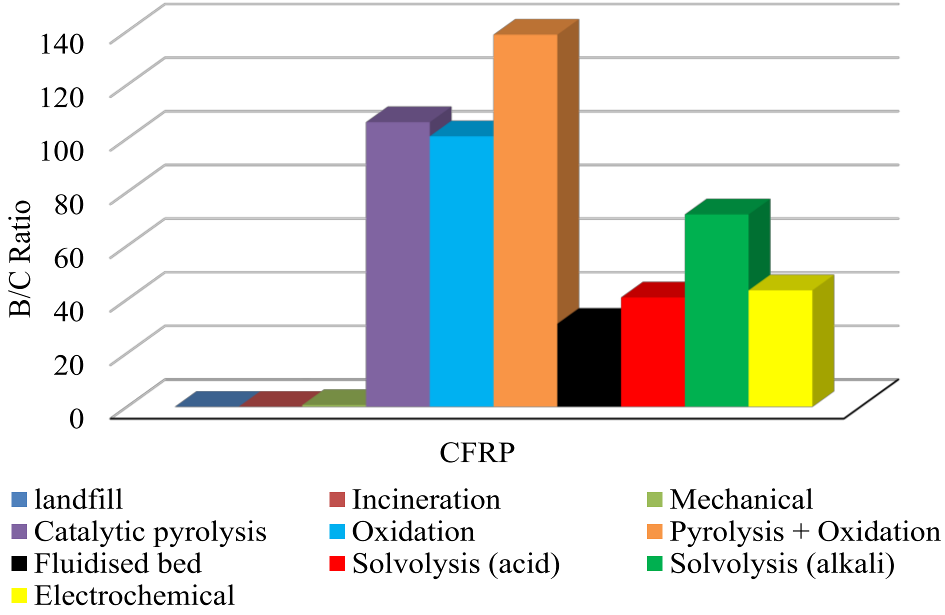
Circular economy

- Revitalise the economic value of carbon fibre in composites
- Reduce the cost for FRP manfacuting

Social, economic and commercial benefits

- More suited for medium and even small-sized businesses, as equipment and operating costs will be reduced compared to existing methods

Research Background



Considering NPV and BCR analysis results for CFRP recycling methods, pyrolysis combined with oxidation could achieve greatest profitability rate with lower expenditure (i.e. higher BCR) while alkali solvolysis can achieve the highest total net profit value with higher expenditure[2].

[2] Wei, Y. and Hadigheh, S. A. (2022). Cost benefit and life cycle analysis of CFRP and GFRP waste treatment methods. Construction and Building Materials, Volume 348, 128654, https://doi.org/10.1016/j.conbuildmat.2022.128654.

CFRP Recycling

- Arrhenius-type kinetic analysis and FRP thermal degradation mechanisms
- Developing a CFRP thermal degradation process via parameter optimisation and investigating the properties of recycled carbon fibres
- Selection of the pre-treatment medium based on the kinetic behaviour and mechanical properties of recover fibres
- Optimisation of heating system applied during the pre-treatment stage
- Development of an innovative thermo-chemical recycling method

CFRP Recycling

Arrhenius-type kinetic analysis and FRP thermal degradation mechanisms

Coats-Redfern method

$$ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2R\bar{T}}{E}\right)\right] - \frac{E}{RT}$$

Friedman method $ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = ln[A(1-\alpha)^n] - \frac{E}{RT}$

OFW method $ln\,\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E}{RT}$

KAS method $ln\frac{\beta}{T^2} = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT}$

Straink method $ln\left(\frac{\beta}{T^{1.92}}\right) = -1.0008\frac{E}{RT} + C$

Coats-Redfern method

Friedman method; OFW method
KAS method; Straink method

model-fitting method

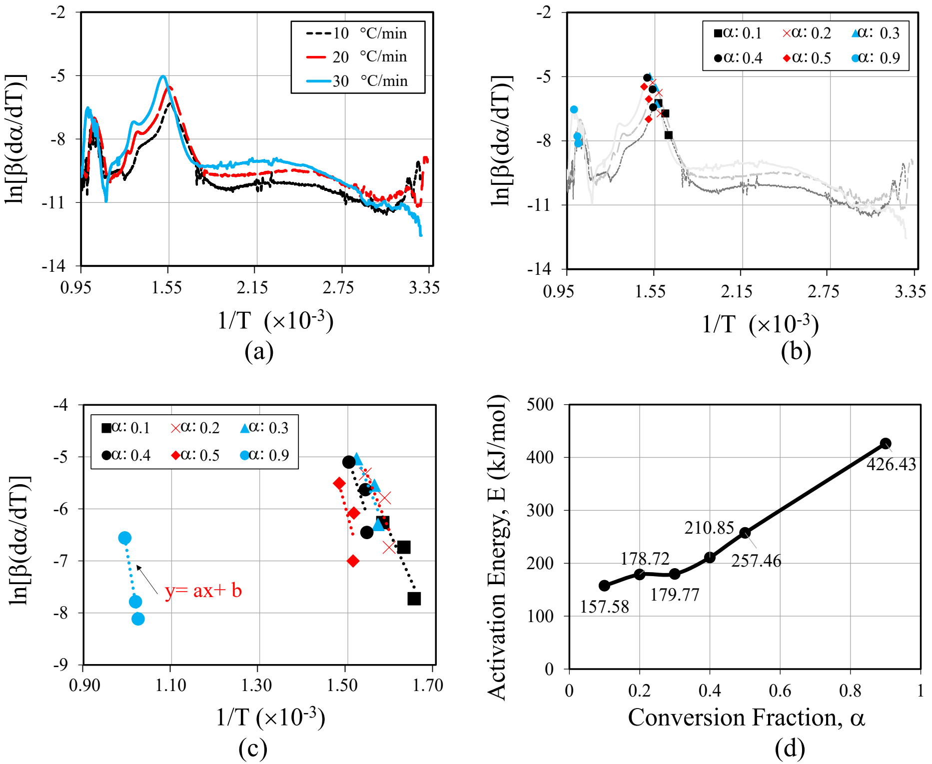
- Discover the effects caused by changing heating rate
- More accurate result for the specific heating condition

VS

model-free methods

- Simplify investigation process
- Reduce the assumption errors made before operating the experiments

CFRP Recycling



(a) ln (β dα/dT) versus 1/T, (b) lining up the data for three heating rates for the same conversion fraction (α), (c) determining the slope of regression line for each conversion (values of a, b and R^2 are shown in Table 2), (d) Friedman method result: activation energies at different conversions.

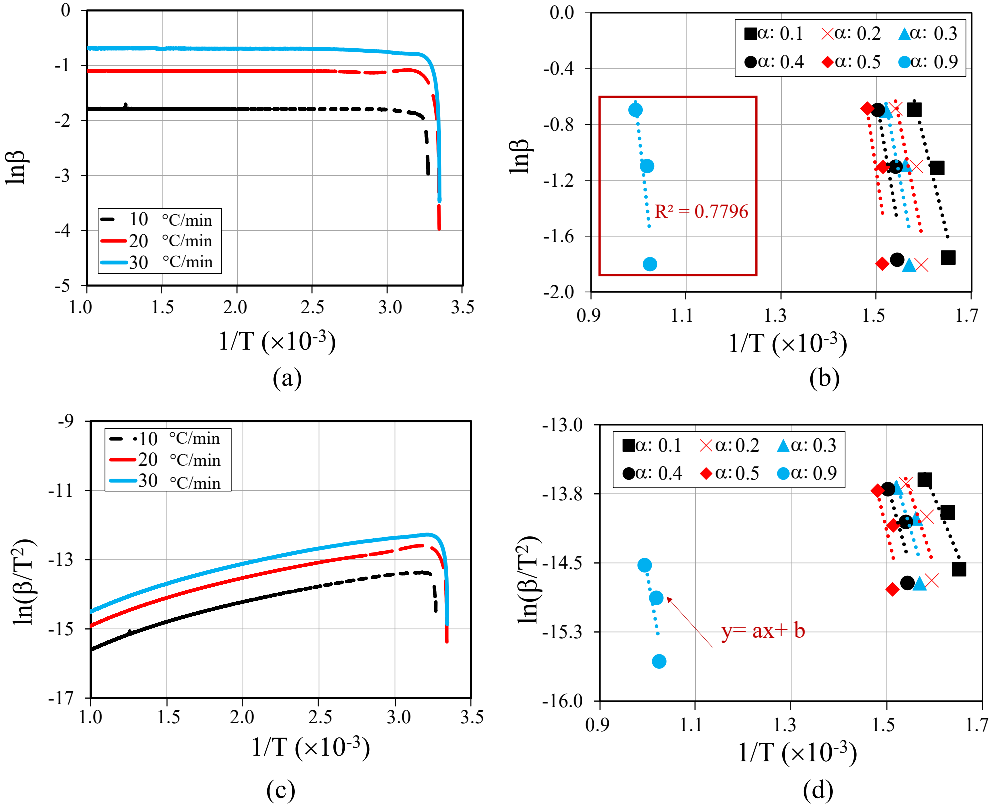
Trendline parameters (slope, a, and x-interception, b) and R2 values correspond to conversion fractions in Friedman method

Conversion Fraction, α	**For figure (c)**		
	a ($\times 10^4$)	b	R^2
0.1	-1.90	23.78	0.85
0.2	-2.15	27.85	0.74
0.3	-2.16	27.88	0.79
0.4	-2.53	33.03	0.71
0.5	-3.10	40.32	0.58
0.9	-5.12	44.40	1.00

Friedman method

$$ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = ln[A(1-\alpha)^n] - \frac{E}{RT}$$

CFRP Recycling



(a and b) Results derived from OFW and (c and d) KAS method; (a and c) Ln(β/T^2) versus 1/T, and (b and d) regression lines corresponding to each conversion fraction (values of a, b and R2 are shown in Table 2).

Trendline parameters (slope, a, and x-interception, b) and R2 values correspond to conversion fractions in KAS method

Conversion Fraction, α	**For figure (d)**		
	a ($\times 10^4$)	b	R^2
0.1	-2.16	18.26	0.54
0.2	-1.86	14.27	0.66
0.3	-1.72	12.47	0.71
0.4	-1.61	11.17	0.75
0.5	-1.27	6.52	0.88
0.9	-2.89	14.21	0.76

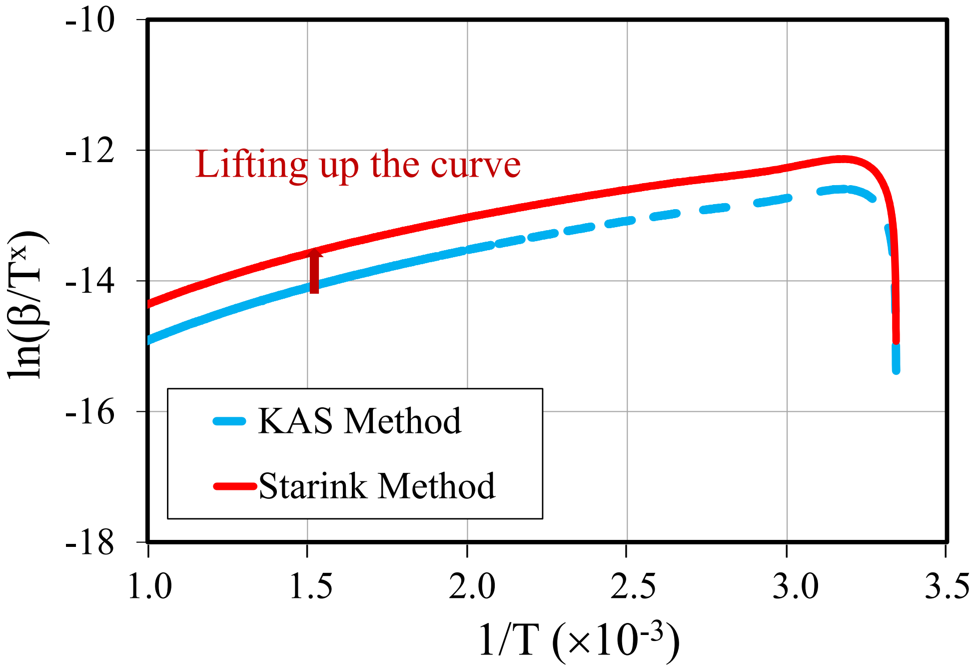
OFW method

$$\ln\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E}{RT}$$

KAS method

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT}$$

CFRP Recycling



Starink method

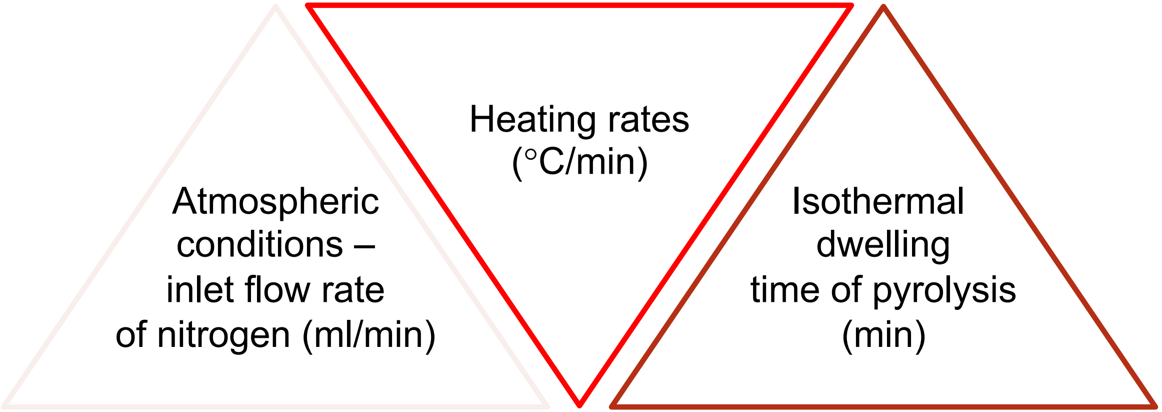
$$ln\left(\frac{\beta}{T^{1.92}}\right) = -1.0008\,\frac{E}{RT} + C$$

- Starink method follows the same approach as that of KAS method but redefines the preliminary assumption of E/RT_f based on the experimental results of solid-state thermal decomposition reaction.
- This approximation results in the adjustment of exponent parameter of T from 2 to 1.92, which can be reflected in curve lifting of $\ln(\beta/T^x)$ versus 1/T.
- This modification can provide more accurate result for FRP composite decomposition kinetics.

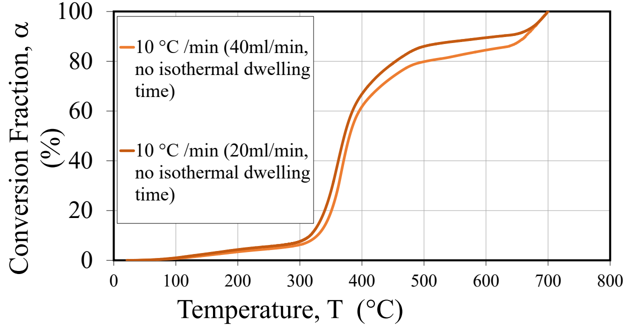
[3] Hadigheh, S. A., Wei, Y. and Kashi, S. (2021). Optimisation of CFRP composite recycling process based on energy consumption, kinetic behaviour and thermal degradation mechanism of recycled carbon fibre. *Journal of Cleaner Production*. Volume 292, 125994, https://doi.org/10.1016/j.jclepro.2021.125994.

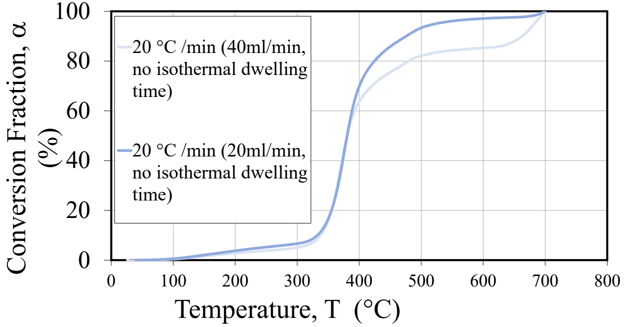
CFRP Recycling

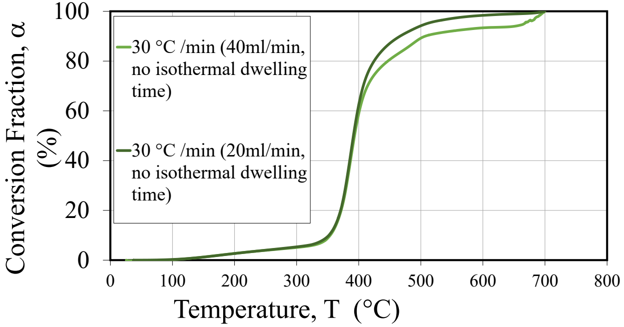
Developing a CFRP thermal degradation process via parameter optimisation and investigating the properties of recycled carbon fibres

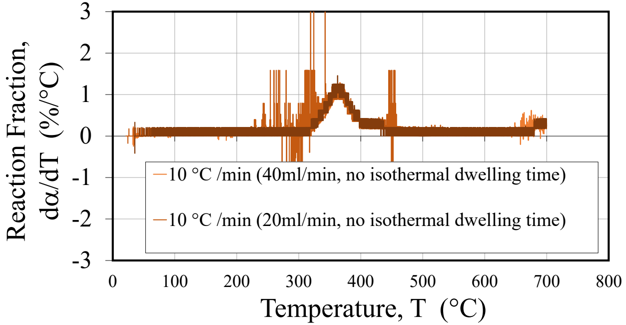


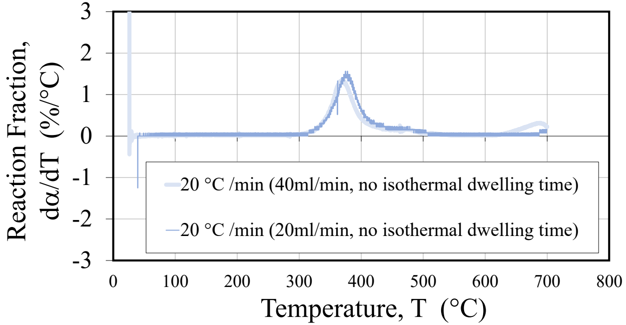
CFRP Recycling

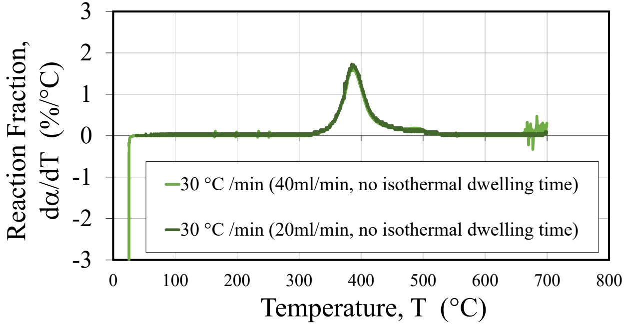




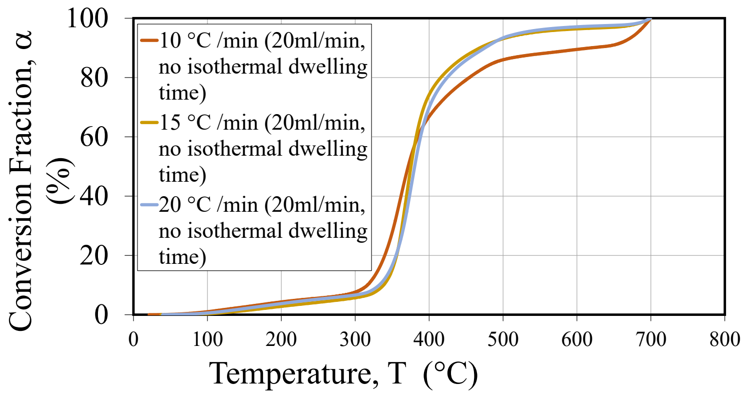


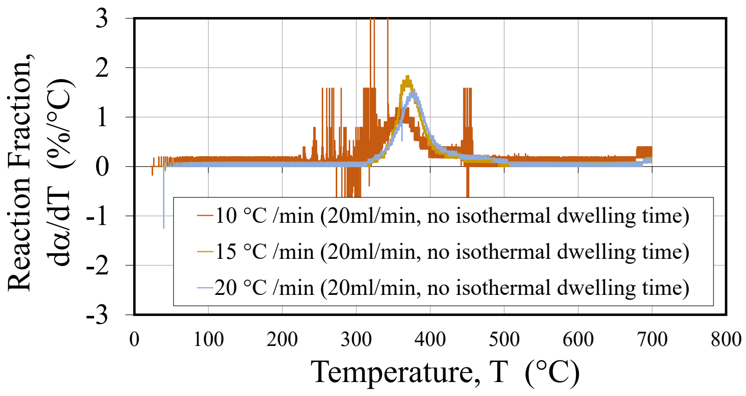


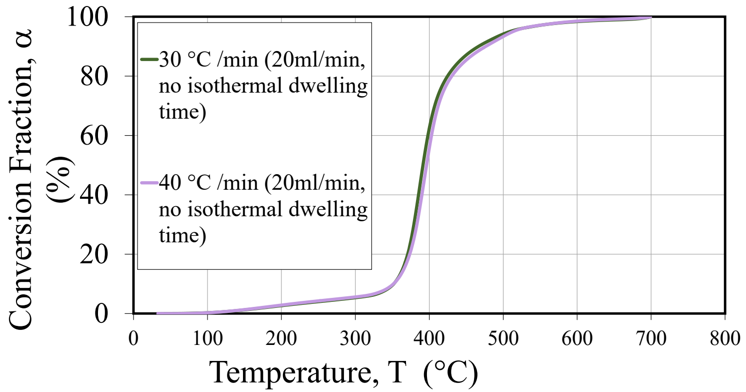


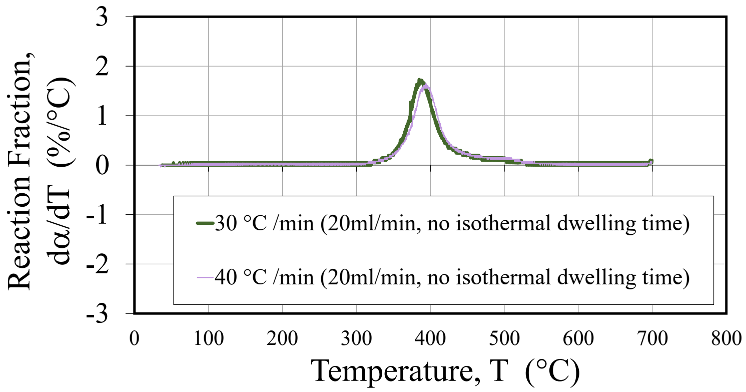


CFRP Recycling

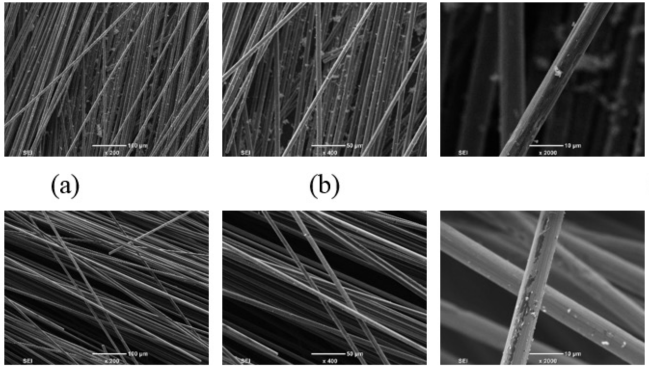








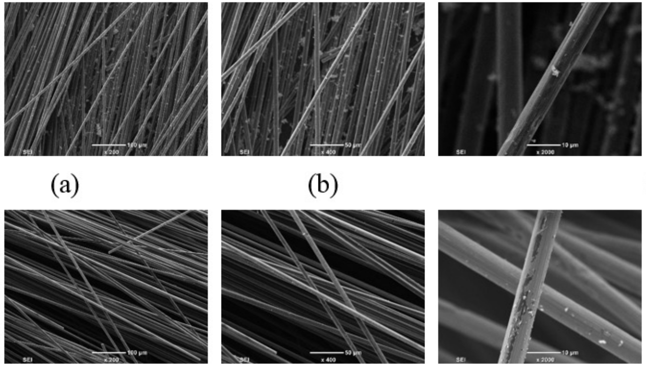
Surface Characteristics



(a) (b) (c)

(d) (e) (f)

SEM images of fibres: (a), (b) and (c) show fibres treated with pyrolysis only (fibres heated to 800 °C at 30 °C/min heating rate and 60 min isothermal dwelling time); (d), (e) and (f) show fibres treated with effective pyrolysis and oxidation (fibres heated to 425 °C under nitrogen and then oxidised at temperatures up to 550 °C at 15 °C/min heating rate and 60 min isothermal dwelling time).



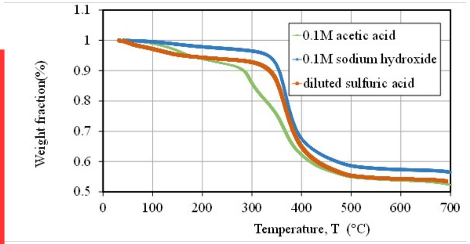
(a) (b) (c)

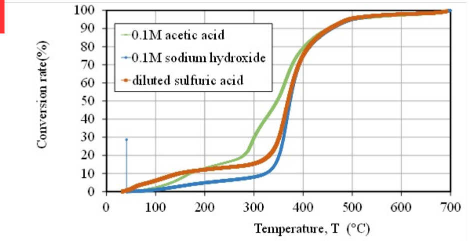
(d) (e) (f)

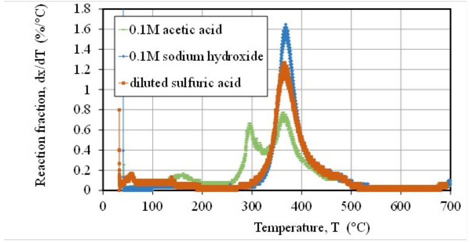
SEM images of fibres: (a), (b) and (c) show fibres treated with pyrolysis only (fibres heated to 800 °C at 30 °C/min heating rate and 60 min isothermal dwelling time); (d), (e) and (f) show fibres treated with effective pyrolysis and oxidation (fibres heated to 425 °C under nitrogen and then oxidised at temperatures up to 550 °C at 15 °C/min heating rate and 60 min isothermal dwelling time).

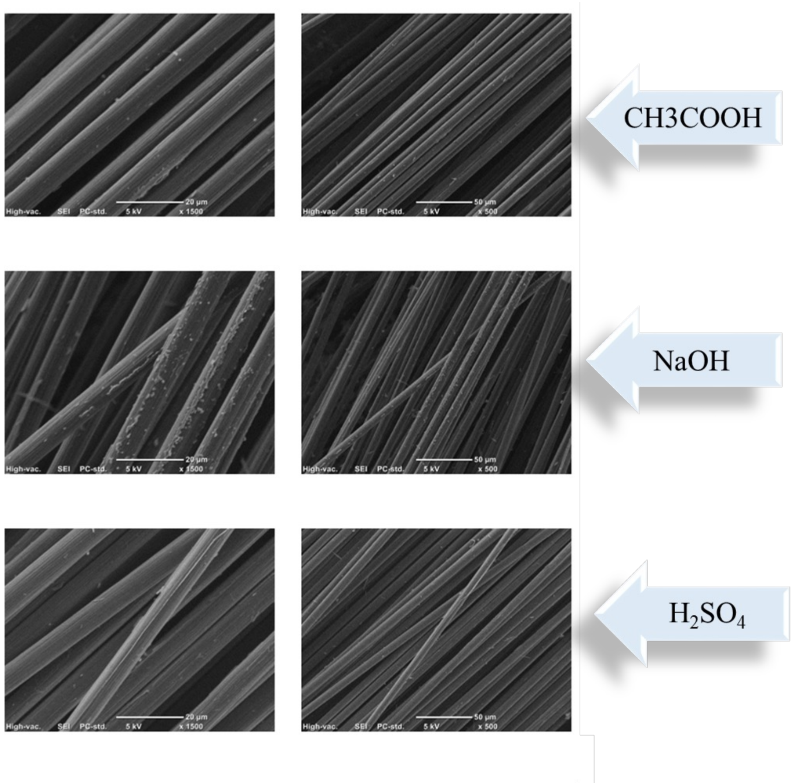
CFRP Recycling

Selection of the pre-treatment medium based on kinetic behavior and mechanical properties of recovered fibres

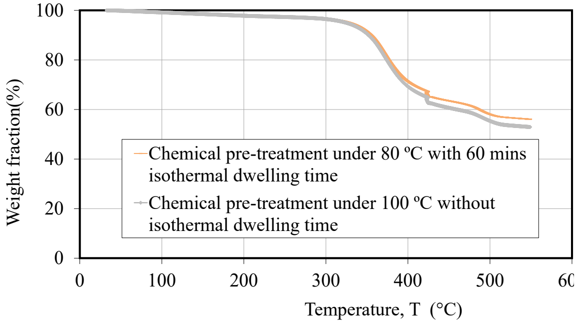


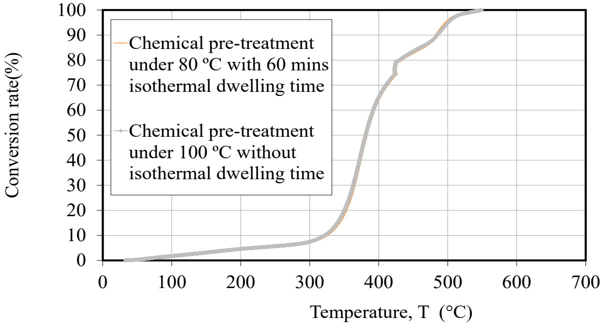


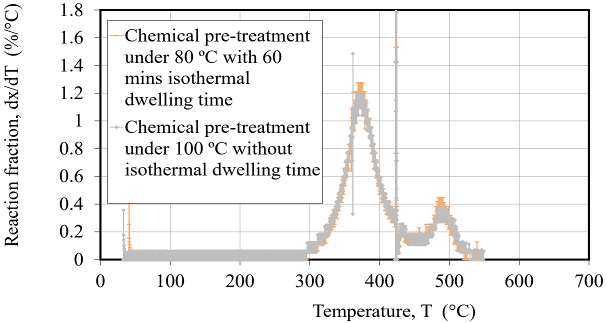


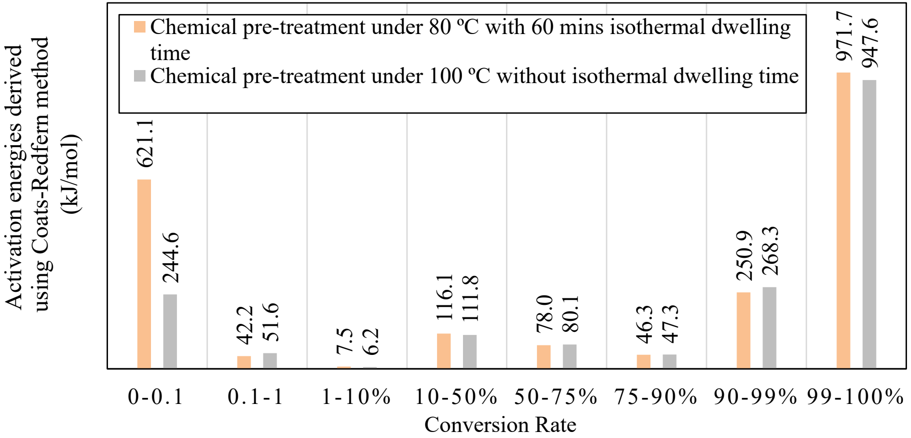


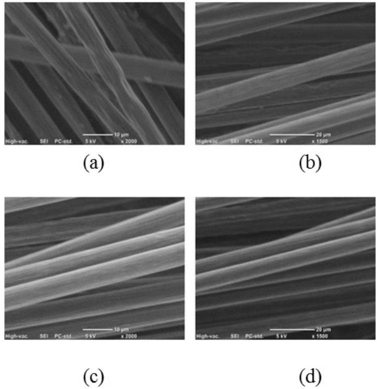
CFRP Recycling





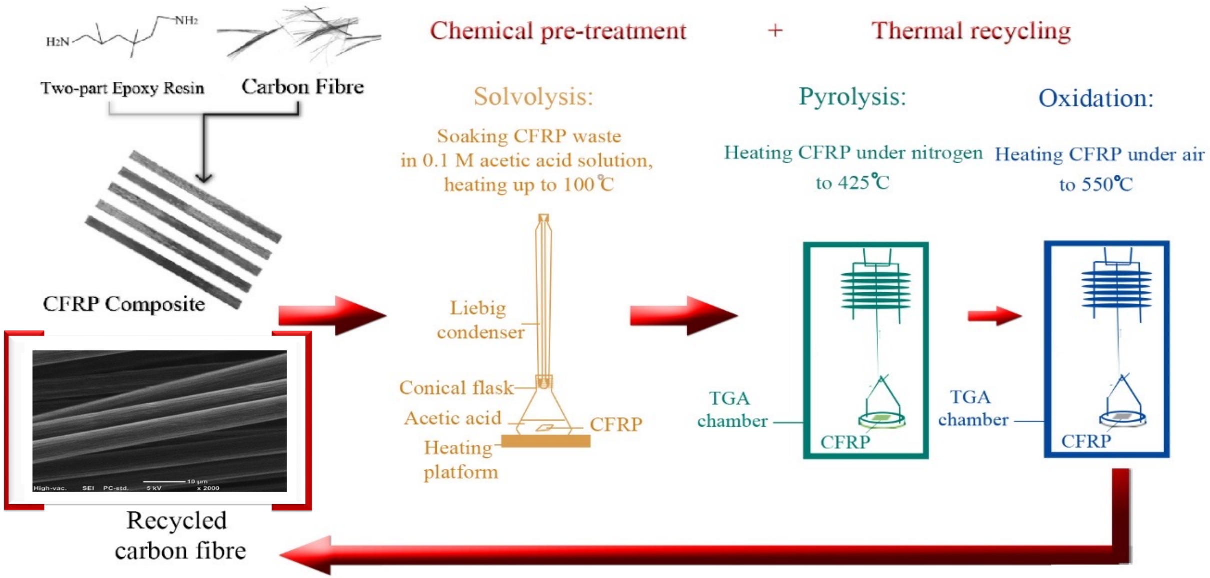






SEM images of fibres recovered with different pre-treatments: (a) and (b) for heating up to 80 °C with 60 mins isothermal dwelling, (c) and (d) for heating up to 100 °C without isothermal dwelling

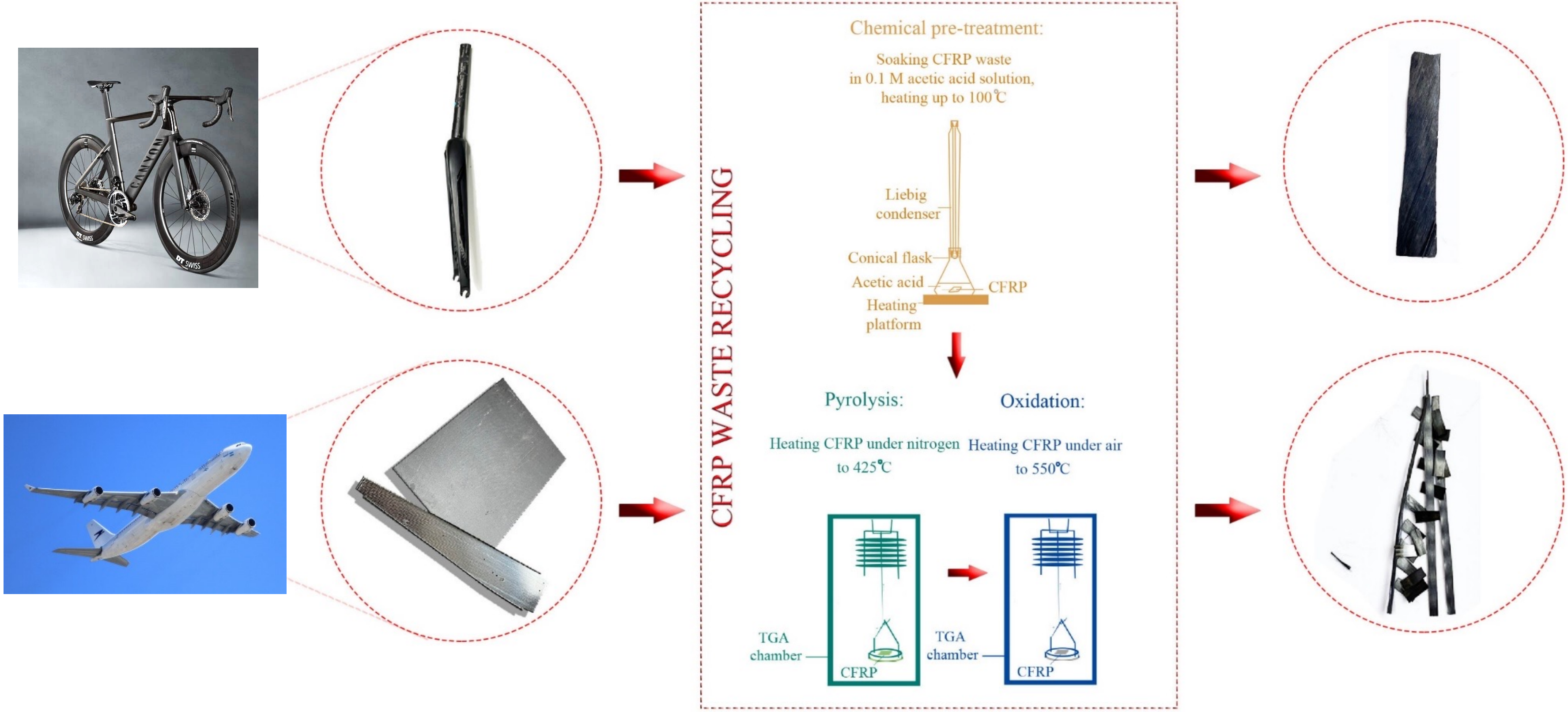
CFRP Recycling



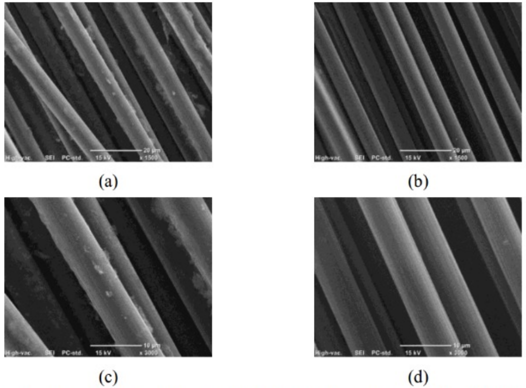
The strength of the recycled fibres was preserved at over 90% of their virgin state, which is 10.21% higher than the strength of recycled fibres recovered via thermal degradation only.

[4] Wei, Y. and Hadigheh, S. A. (2023). Development of an innovative hybrid thermo-chemical recycling method for CFRP waste recovery, Composites Part B: Engineering, Volume 260, 110786, ISSN 1359-8368, https://doi.org/10.1016/j.compositesb.2023.110786.

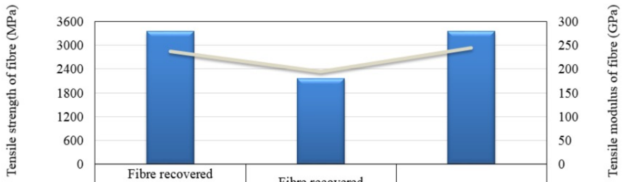
Practical Application



Practical Application

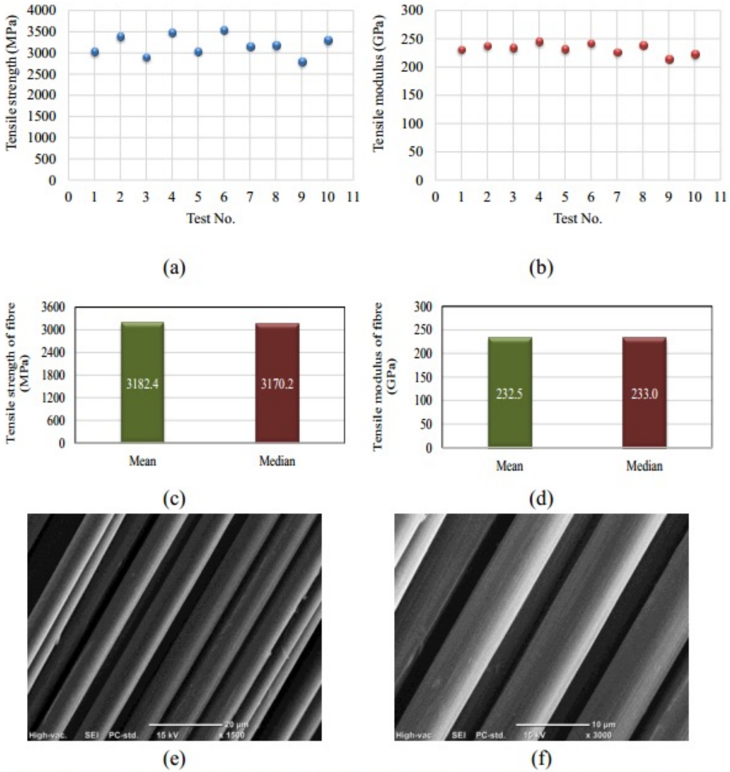


Recovered carbon fibre from (a) and (c) bike fork with coating and (b) and (d) bike fork without coating (coating removed via fine graded polishing) prior to recycling process



	Fibre recovered from middle layer of polished bike waste	Fibre recovered from top layer of polished bike waste	Untreated bike waste (with coating)
Tensile strength （MPa）	3353.4	2166.9	3356.1
Tensile modulus （GPa）	236.5	195.2	243.9

Average tensile strength and tensile modulus of different recycled fibres



Tensile strength (a and c) and modulus (b and d) of recovered fibres from airplane wastes, and (e and f) SEM images with magnification of (e) ×1500 and (f) ×3000

Conclusions

- A closed-loop CFRP life cycle can reduce pollution by decreasing waste disposal, maximise material use and save energy. This contributes to the circular economy and environmental protection.

- To optimise CFRP composite recycling, energy consumption, kinetic behaviour and thermal degradation mechanism during pyrolysis were studied.

- The proposed recycling procedure includes solvolysis pre-treatment of CFRP at 100 °C, followed by pyrolysis up to 425 °C and oxidation up to 550 °C with a heating rate of 15 °C /min.

- Additional solvolysis procedure can increase retention of fibre's mechanical properties by decreasing heat consumption during recycling. When proper pre-treatment was used prior to thermal deterioration, the strength of recycled fibres can be preserved at over 90% of their virgin state.

- By putting this technology in practise, the results of recycling bicycle and aircraft components demonstrated that the parameters must be slightly altered for various types of CFRP based on the matrix type. In addition, the coating should be thoroughly removed from the components prior to waste recycling to prevent major fibre damage during the polishing process.

Acknowledgement

Contact us:

Yaning Wei (yaning.wei@sydney.edu.au)
Ali Hadigheh (ali.hadigheh@sydney.edu.au)