



Development of an innovative hybrid thermo-chemical recycling method for CFRP waste recovery

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ARTICLE INFO

Handling Editor: Dr Uday Vaidya

Keywords:

Thermal analysis
Hybrid recycling
Carbon fibre
Mechanical testing

ABSTRACT

Disposal of carbon fibre reinforced polymer (CFRP) waste in landfill is a significant environmental issue. Cost-benefit and life cycle assessments have demonstrated that pyrolysis and chemical recycling are among the most effective waste treatment strategies. This paper presents the development of a novel low-temperature pyrolysis combined with solvolysis pre-treatment as an effective recycling method for CFRP composite wastes. In this research, the process parameters were meticulously determined to ensure the simultaneous achievement of increased material utilisation and energy efficiency. The kinetic analysis results demonstrate that the pre-treated CFRP, unlike its untreated counterparts, displays an additional preliminary reaction stage, facilitating a higher level of breakdown at lower temperatures. Moreover, solvolysis pre-treatment increased retention of the fibres' mechanical properties by reducing the heat consumption during recycling. With a proper pre-treatment prior to thermal deterioration, the strength of the recycled fibres was preserved at up to 90.53% of their virgin state, which is 10.21% higher than the strength of recycled fibres recovered via thermal degradation only. To demonstrate the practicality of this research, a commercial bike's fork and airplane scraps made of CFRP composites were successfully recycled using the hybrid approach developed in this research. The results validate the effects of chemical pre-treatment and also demonstrate the efficacy of coating removal on the mechanical characteristics of carbon fibres recovered from various types of CFRP for real-world applications.

1. Introduction

Carbon fibre reinforced polymer (CFRP) is a type of anisotropic composite that is used in a variety of industries because of its exceptional mechanical properties and environmental wear resistance. The global demand for carbon fibre reinforced polymers has surged with an approximate annual growth rate of 12.5% over the past two decades, at the same time, this high demand has also resulted in the generation of a significant amount of waste associated with CFRP production processes [1]. CFRP waste is non-biodegradable and if it is dumped in landfill without being given the appropriate treatment it can cause harm to the environment. It is projected that the worldwide annual accumulation of carbon fibre reinforced polymer waste will rise to 20 kilotons by the year 2025 if suitable recycling methods are not adopted [2]. The estimated amount of waste carbon fibre could reach 263,000 tonnes in the year 2030, which could lead to a more serious escalation of this problem [3]. It is optimal to establish a closed-loop life cycle for CFRP composites because doing so is the best way to reduce industrial pollution while also increasing material use and energy efficiency [4]. To achieve a closed

loop life cycle for CFRP composites successfully, carbon fibre recycling, realignment of recycled fibres, remanufacturing and application of recycled CFRP are the four fundamental pillars that are needed to be carefully designed and developed. In the process of fibre recycling, carbon fibre is extracted from waste CFRP by stripping away the resin that coats the surface of the fibre. Mechanical, thermal, chemical and thermo-chemical approaches are the four primary categories of fibre recovery methods. Cost-benefit analysis and life cycle assessments were conducted to find the optimal waste management strategy for fibre-reinforced polymer. The results indicate that chemical recycling is an attractive strategy for mitigating environmental consequences and maximising economic advantages [5].

Chemical recycling is a method for recovering fibre by dissolving the matrix of fibre-reinforced composites in a liquid via a chemical reaction between the matrix and solution [6]. For solvolysis at low temperatures, the environment in which the solution is handled must be lower than 200 °C. Liu et al. used a nitric acid solution that was heated to 90 °C to study CFRP degradation. The results indicated that an epoxy resin matrix may be broken down into low-molecular-weight compounds and

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<https://doi.org/10.1016/j.compositesb.2023.110786>

Received 3 March 2023; Received in revised form 1 May 2023; Accepted 2 May 2023

Available online 3 May 2023

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that insoluble carbon fibre can be recovered using low-temperature solvolysis. The reduction in tensile strength of recovered single carbon fibre ranged from 1.1 to 13.4%. Nevertheless, the recycling procedure for microscopic samples takes over 100 h, makes it inappropriate for the use in industrial scale. The findings provide new insights into the influence that certain qualities have on reaction behaviour [7]. The temperature at which the reaction occurred is one of the most important parameters in reaction process, followed by the ratio of the sample weight to the volume of the solution and then the solution's concentration. In another research [8], a Teflon circulating-flow reactor was utilised to decompose composites made of 52% carbon fibres, 8% glass fibres, and 40% matrix. The degradation occurred over 8 h in a temperature of 90 °C. After purging the oxygen with nitrogen gas, a nitric acid aqueous solution was pumped into the circulating flow reactor. By using this technique, unanticipated byproducts such as pyrolytic carbon could be avoided entirely. In this research, the effects of the flow rate of the circulating solution, the temperature at which the breakdown occurs and the concentration of the reaction solution on recycled fibres were investigated. The loss in tensile strength of recycled single carbon fibre was reported 2.91%; nevertheless, small amount of matrix contamination may still be visible using SEM.

Xu et al. attempted to reduce the duration of recycling process in low-temperature solvolysis [9]. First, the composites were treated in acetic acid at a temperature of 120 °C for 30 min to offer a higher surface area. Hence, the composite could be stacked and inflated, which led to faster degradation process. They heated a solution comprising 50% hydrogen peroxide (H₂O₂) and 50% N, N-dimethylformamide up to 90 °C for 30 min inside a synergistic oxidative degradation system to recover clean fibres. The matrix decomposition ratio was more than 90%, and fibres with a tensile strength more than 95% of the original carbon fibre were obtained after recycling. Despite the surface's smoothness, residuals (undecomposed resin) were observed on recovered carbon fibres. In addition, Kim et al. extracted clean and short recovered carbon fibre from the oxidative breakdown of cross-linked epoxy resin by using potassium permanganate (KMnO₄) solution, followed by acid treatment at a low temperature [10]. The degree of depolymerization can rise from 46% to 95% if the composites are immersed in the KMnO₄ solution for 120 min as opposed to being removed immediately. With this method, they could retain tensile strength of recycled fibre up to 90.7% compared to those of virgin fibre. Regarding the surface characteristics, very small amount of matrix was observed on the fibre after recycling; nonetheless, traces of oxygen and manganese were discovered. This suggest that more treatment is required before the FRP remanufacturing process can be carried out.

Combining chemical recycling with other techniques can offer several advantages over solvolysis alone, including fewer operational constraints. Two co-systems have gained popularity: one uses intense oxidation, while the other employs a combination of electrolytic processes and chemical degradation. In the co-system with intense oxidation, specimens containing sulphuric acid solution are rapidly oxidised to reach a temperature of 110 °C. To enhance the process and increase productivity, H₂O₂ is added to the solution once it reaches boiling point. On average, the recycling process takes a few hours to complete, with an additional hour required for filtering and drying in the oven [11,12].

In contrast, electrolytic and chemical degradation processes uses a mild reaction environment with an electrolytic system [13]. This system recovers fibres from waste CFRP by reacting it with a neutral solution at room temperature, consuming less energy and having fewer detrimental effects on the environment [14]. The system consists of a DC power source, a CFRP anode, and a steel cathode. CFRP is submerged in a sodium chloride (NaCl) solution at room temperature for 21 days to complete the electrolytic reaction of the matrix. During this time, the temperature and relative humidity are kept constant. Afterward, the carbon fibres are subjected to 50 °C temperatures for few days. The tensile strength of recycled carbon fibre can range between 53% and 80% of that of virgin carbon fibre [15]. The tensile capacity of recycled

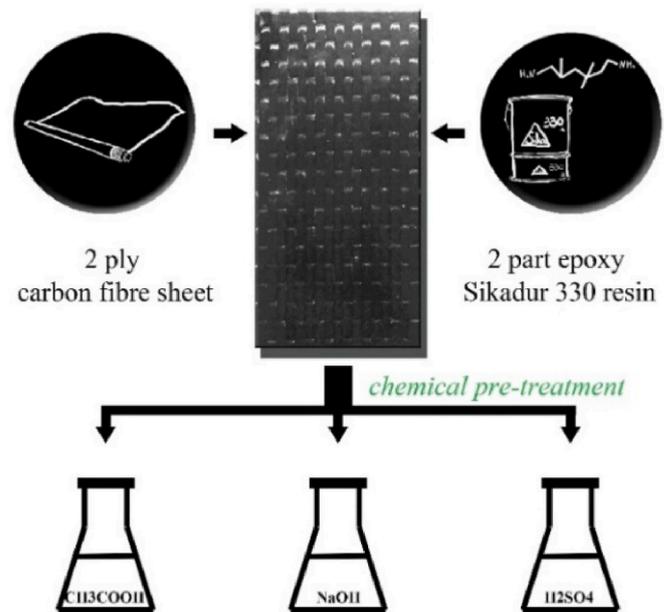


Fig. 1. CFRP sample preparation.

carbon fibre is affected by the concentration of the solutions used to recycle it: a higher concentration of NaCl solution can diminish the tensile strength of fibres while leaving the surface of fibres clean [16, 17].

In comparison with other chemical recycling technologies (e.g. chemical processes combined with electrical techniques, subcritical and supercritical recycling), low-temperature solvolysis offers a greater control over the chemical reaction and does not result in any unanticipated oxidation reactions throughout the recycling process [6,18–21]. In addition, low-temperature solvolysis is advantageous for high economic return and the establishment of a material's sustainable development as a result of its low capital expense and reduced consumption of both non-renewable and renewable energies [10,11,15,17]. However, its lengthy recycling period and lower recycled-fibre quality may lead to unconfirmed commercial acceptability [22]. The low quality of fibres may present itself in either surface topography and/or mechanical behaviour [9,15,23].

It is vital to design a chemical recycling technology that is more suitable for commercial investors by evaluating how to maximise the advantages of low-temperature solvolysis while minimising its disadvantages in relation to long processing time. Applying chemical recycling techniques as the pre-treatment for thermal recycling operations may produce high-performance recovered carbon fibres while simultaneously decreasing the required capital investment and enhancing production efficiency. This is due to the fact that pre-chemical recycling processes can decompose the matrix primarily and initiate fibre-matrix debonding to facilitate rapid heat transfer at the start of thermal recycling processes. Therefore, in this paper, we will develop an innovative thermo-chemical recycling method for FRP waste recovery via considering different chemical pre-treatments. The optimisation of the pre-chemical treatment parameters, such as the type of solution employed and the temperature at which the treatment is completed, will be facilitated by the TGA, SEM, and tensile tests on recycled fibres. This study also focuses on the real-world application of this established technique, which is the recycling of a decommissioned commercial bicycle component and composite waste from an airplane component. This provides valuable practical information about the performance of the proposed method for industrial applications by revealing the effect of coating and types of composites on the thermal degradation process.

Table 1

Characteristics of the virgin carbon fibre and epoxy used to manufacture composite specimens.

Carbon fibre					
Material Property	Areal weight (g/m ²)	Tensile modulus (GPa)	Tensile strength (MPa)	Nominal thickness (mm/ply)	Density (g/cm ³)
Value	300	210	3000	0.12	1.79
Epoxy adhesive					
Material Property	Viscosity - Shear rate (c/s)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break	Density (kg/l)
Value	50	4.5	30	0.9% (7 days at +23 °C)	1.30 ± 0.1

2. Experimental design and methodology

2.1. Specimen fabrication

The wet layup technique was used for manufacturing of the carbon fibre-reinforced composites. The material was fabricated by stacking two plies of unidirectional carbon fibre mat with a tensile strength of 3000 MPa, a thickness of 0.24 mm and a density of 1.79 g per cubic centimetre. The epoxy resin Sikadur 330, with a density of approximately 1.3 g/cm³, was used in the mixing process. The matrix was prepared by combining the hardener (trimethyl hexamethylene diamine) and the base (trimethyl hexane) in a 1:1 ratio. After the matrix had been infused into the fibre layers, a vacuum pump and roller were used to reduce the amount of excess resin and air bubbles. The curing process for the composites last one week and occurred in ambient temperature. The weight fraction of CFRP composites was 45%, as shown in Fig. 1. Table 1 presents further properties of the virgin carbon fibre and matrix used to fabricate composite specimens. A low-temperature solvent was used as a pre-treatment method prior to the primary recycling process. Three different solutions were used, including diluted sulphuric acid (20 wt % H₂SO₄), weak acetic acid (0.1 N CH₃COOH), and weak sodium hydroxide (0.1 N NaOH), all of which were created by Titripur®. To preliminarily degrade the internal bonding structure of the matrix, samples were stored at room temperature for 132 h after being soaked in the solutions separately. Following the completion of the solvolysis process, samples were taken from the solutions and allowed to reach a dry condition at room temperature for about 15 h.

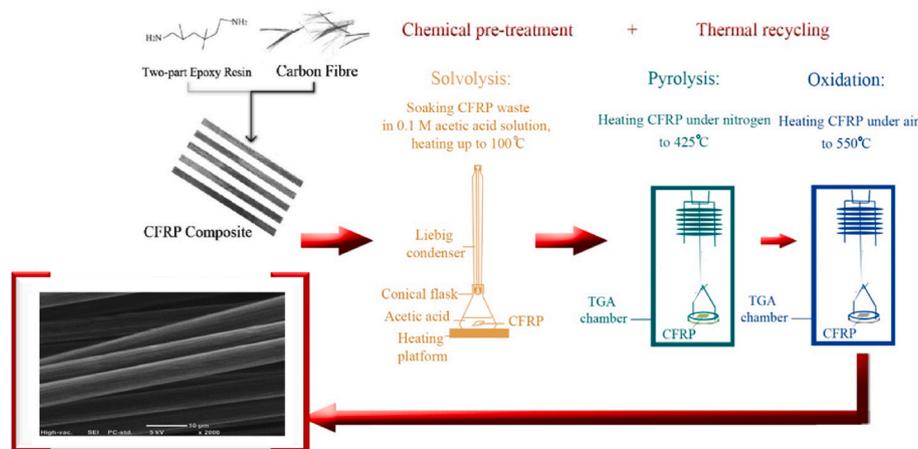
To improve economic efficiency and productivity, the operating duration involved in the pre-treatment process needs to be optimised. Hence, a heating process was implemented to boost the matrix decomposition. A heating platform was placed beneath the 1000 ml Erlenmeyer conical flask containing the specified solution and CFRP waste to increase the temperature and accelerate the reaction. The flow inlet and outlet were equipped with a B24/600 mm Liebig condenser, which was

used to cool the gaseous material and convert it into a liquid that could be returned to the flask. This helped to maintain the concentration of the solution consistent. Eighty degrees Celsius with 60 min of isothermal dwelling and 100 °C without isothermal dwelling were the two distinct conditions that were evaluated. Once the heating procedure was finished, the sample and solution were allowed to cool down until they were at room temperature. After filtering the liquid using a funnel and laboratory filter paper, the treated composite samples were collected. Before the TGA testing, samples were dehydrated for 15 h in ambient temperature.

2.2. Thermal degradation of pre-treated CFRP

To evaluate the composites' mass losses throughout the thermal degradation process of pre-treated CFRP samples, a thermal gravimetric analyser model Q50 was utilised. This analyser has a temperature range for heating that goes from 20 °C to one 1000 °C, and the heating rate may vary anywhere from 0.1 °C per minute to 100 °C per minute. The temperature readings have an accuracy of within 0.01 °C, while the weighing measures have an accuracy of within 0.1 g. A platinum TGA pan with a diameter of 10 mm was utilised for the purpose of storing samples within the high-temperature environment of the heating chamber. The whole procedure of thermal recycling was recorded, and the data was sent to the attached computer. Calculations were carried out to determine the average conversion per cent and the reaction rate using repeated samples. The entire thermal degradation procedure consisted of three phases: (i) preliminary evaluation of thermal deterioration during the pyrolysis process for CFRP treated with various solutions, (ii) a comprehensive examination of a hybrid thermo-chemical recycling system involving the improved chemical pre-treatment, pyrolysis, and oxidation process, and finally (iii) applying the developed technology on real decommissioned CFRP composites.

During Phase 1, the CFRP composite coupons pre-treated with three different solutions were cut into square shapes before being heated in a pyrolysis environment set to a temperature of 700 °C and contained a

**Fig. 2.** Thermo-chemical recycling method.

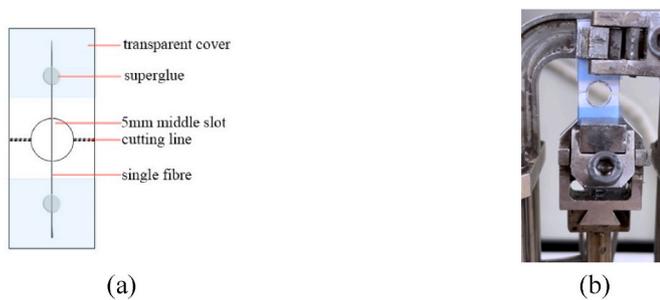


Fig. 3. (a) Paper coupon, and (b) single-fibre tensile tests performed via DMA 2980 dynamic mechanical analyser.

flow of nitrogen gas at a rate of 20 mL per minute. The rate of heating was 15 °C per minute. In Phase 2, the recycling process was optimised by exploring two heating scenarios: 80 °C with an isothermal dwelling time of 60 min and 100 °C without an isothermal residence. Subsequently, an enhanced thermal recycling procedure (pyrolysis combined with oxidation) which was initially proposed by the authors [24] and subsequently refined, was used to remove matrix and restore high-quality fibres. This method includes pyrolysis up to 425 °C and secondary oxidation up to 550 °C. A stage of equilibrium enables the entire transformation of the atmosphere from nitrogen gas to air after a given amount of time. During Phase 3, the optimised hybrid thermo-chemical recycling process was used to recycle the fork of a commercial bicycle and airplane scraps made of CFRP composites in order to validate the performance of the proposed recycling technology in practical applications. The whole process of developed thermo-chemical recycling method is shown in Fig. 2.

2.3. Properties of recycled carbon fibre

Mechanical and physical characteristics of recycled fibres were examined using tensile testing and scanning electron microscopy. The surface morphology of the fibres recovered from pyrolysis was analysed by performing SEM tests to determine the effect of the various solutions on the quality of the recycled product. This analysis included the amount of char, the amount of fibre fracture, and the reduction in the average diameter of the fibre. SEM images of recycled fibres were taken via Tabletop NeoScope. Conductive carbon tapes were applied to the SEM metallic stub in order to retain the recycled fibres in place. To reduce the sample's unstable charge and improve electromagnetic detection, three thin gold coatings were added. By optimising the focus and sigma, the angle of the sample's position, the brightness of the picture, and the speed of the electro-scanning, images of fibres with varied magnitudes were acquired.

TA Instruments DMA 2980 dynamic mechanical analysers were used to perform single-fibre tensile tests on coupon samples. To reduce post-process damage from friction between the container and the collected recycled sample and hence the error in test findings, a single recycled fibre was chosen at random from the centre of the recycled fibre bundle for production of the coupon sample. Prior to making the samples for tensile tests, the diameter of each recycled fibre was determined using scanning electron microscopy. Superglue was used to secure the fibre to a thick paper coupon. The coupon had overall measurements of 25 mm × 10 mm with a hole size of 5 mm. When loading the sample into the tensile testing equipment, it was imperative that the fibre's axis be parallel to the cross-head. The paper coupon was then slit along the middle line as shown in Fig. 3. To ensure that only the fibre resists the load during the tensile test, the paper coupon was carefully cut along the edge. Following this, a preload of 0.002 N was applied to the fibre to ensure homogeneous stress before running the tensile test. The testing procedure followed ASTM C1557-20 [8], and the cross-head operated at a speed of 0.5 N/min.

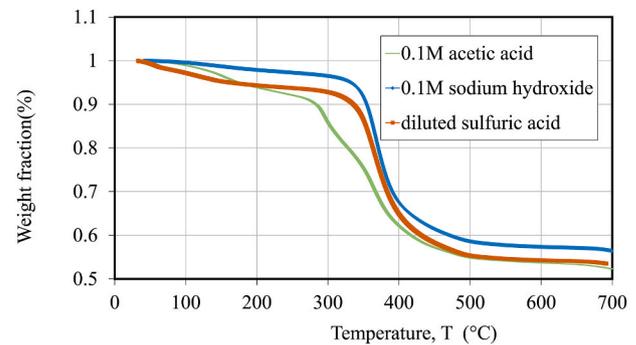


Fig. 4. Weight loss during the pyrolysis process for composites with different pre-treatments.

3. Results and discussion

3.1. Effects of chemical pre-treatment medium on degradation behaviour of composite during pyrolysis

CFRP specimens were separately treated by diluted sulphuric acid, 0.1 M weak acetic acid, and 0.1 M sodium hydroxide for 132 h at room temperature. This process aimed to de-crosslink the matrix from the fibres and create micro-cracks which can provide a larger interface for sufficient heat conduction. This benefits the subsequent thermal degradation decomposition of epoxy by accelerating the degradation process while consuming less energy. Because of the curing process, the bond between the matrix and the fibres in the inner layers of composite is typically weaker than the bond between the matrix and the fibres of outer layers. During chemical pre-treatment stage, solvolysis enables a preliminary debonding to take place between the matrix and the fibre within the outer layers of the composite. In addition, the mass remains approximately the same before and after the pre-treatment since only a small amount of oxidative chemical degradation took place, and the matrix is still present on the composite. The benefits of utilising a low concentration solution are that (i) the treatment solution is weak with lower safety hazards, which suggests that it has the potential to be used in industrial applications without causing significant damage to the environment, and (ii) the solution could be re-used to improve cost-effectiveness.

After solvolysis, pyrolysis up to 700 °C with 15 °C/min was employed, which aims to remove matrix completely and produce clean fibres. Kinetic analysis was carried out in this experiment to accurately assess the impacts of various chemical pre-treatments on the degrading behaviour of composites during pyrolysis. The weight loss data during the CFRP decomposition process was collected and presented in Fig. 4. A more significant portion of the matrix was eliminated from the CFRP that was pre-treated with diluted sulphuric acid before 180 °C compared to those that had any other pre-treatment. This suggests that treatment with sulphuric acid was beneficial for producing increased epoxy breakdown at the start of CFRP thermal deterioration. A more considerable breakdown behaviour was observed due to the acetic acid pre-treatment while the reaction was in its main stage. At a temperature of 330 °C, the weight fraction of CFRP that was treated with acetic acid was 0.795. In contrast, those treated with sulphuric acid and sodium hydroxide, respectively, had weight fractions of 0.905 and 0.951. After 330 °C, the difference in weight fraction between the different approaches begins to reduce and continues until 490 °C. This might be because acetic acid had less effects on the interaction between the matrix and the fibres at the outer layers of composite. However, it still had higher and deeper penetration, which enabled rapid debonding of matrix and fibre within the inner layers of CFRP during thermal degradation. After 490 °C, the change in weight fractions for all samples became gradual and nearly constant. After the process, the relative weight losses for 0.1 M acetic acid, 0.1 M sodium hydroxide, and diluted sulphuric

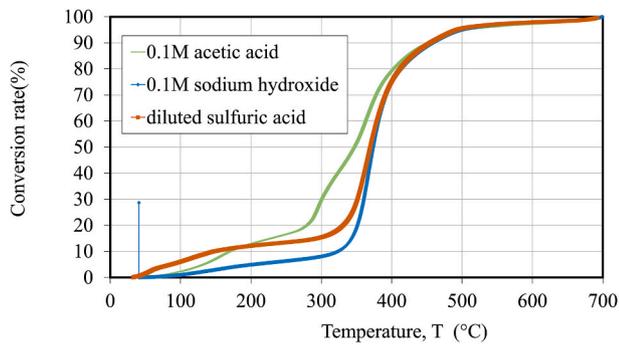


Fig. 5. Conversion rate during the pyrolysis process for composites with different pre-treatments.

acid were 0.47, 0.46, and 0.43, respectively.

Arrhenius type Kinetic analysis, as shown in Equation (1), is a fundamental theoretical technique for studying the kinetic behaviour of material decomposition.

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad (1)$$

where k is the rate constant, T is the temperature, A is a pre-exponential factor, e is Euler's number (2.718), E_a is the activation energy, and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Equation (2) could be used to compute the conversion rate.

$$\alpha = \frac{M_i - M}{M_i - M_f} \quad (2)$$

where M_i is the initial mass, M the transitory mass, and M_f the specimen's post-pyrolysis mass.

In equation (3), the reaction order (n) is another important kinetic parameter that affects fractional decomposition. Equation (4) can be used to calculate the reaction fraction of FRP thermal deterioration by combining the Arrhenius equation with fractional decomposition equations [25]. For modelling kinetic performance, Equation (4) presents the activation energy (E_a) and a pre-exponential component (A) [26].

$$\frac{d\alpha}{dt} = kf(\alpha) = k(1 - \alpha)^n \quad (3)$$

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} (1 - \alpha)^n \quad (4)$$

Results have demonstrated that the pyrolysis of CFRP with pre-chemical treatment is comprised of three primary stages (Fig. 5): stage one, which lasts up to 180 °C and removes a maximum of 10% of the epoxy matrix; stage two occurs during temperatures between 180 °C and 425 °C, which is also the main reaction stage. Finally, the last stage includes temperatures ranging from 425 °C to 700 °C when the remaining (approximately 15%) of matrix and chars are removed. Pyrolytic carbon coated on fibres may lead to the formation of stage 3 decomposition processes. Pyrolytic carbon is a by-product of pyrolysis process which covers the surface of the CF and hinders matrix conversion at low energy levels. By increasing the temperature, the thickness of pyrolytic carbon layer decreases, enabling faster matrix degradation during the subsequent stages.

In contrast to un-treated CFRP, which only has two reaction stages, the pre-treated CFRP demonstrates an additional preliminary reaction stage (stage 1), which enables a higher level of breakdown to occur at lower temperatures. This may be owing to the fact that when the matrix on the surface of the CFRP samples was decrosslinked, cracks were initiated in the matrix which allowed quick heat conduction at the early reaction stage. The conversion fraction increased slightly with a constant rate between 490 °C and 700 °C, implying a steady degradation

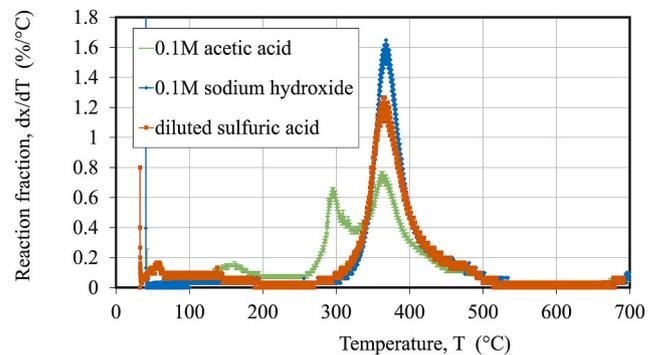


Fig. 6. Reaction fraction during the pyrolysis process for composites with different pre-treatments.

mechanism at the high temperature.

Although the conversion fraction of each specimen was comparable, the behaviour of the main reaction between 180 °C and 425 °C changes based on the type of pre-treatment chemical solution. Applying an alkali solution instead of the acid solution led up to a considerable delay in the matrix conversion, particularly between the temperatures of 250 °C and 340 °C. These delays in conversion are related to diffusion mechanism of pre-treatment solution in CFRP specimens. During the solvolysis process, the de-crosslinking of the matrix begins at the outermost layer and progresses into the inner layers. At the same temperature, sulphuric and acetic acids provide the greater level of primary de-bonding between matrix and fibres. Hence, distinct behaviours in the deterioration of the internal matrix occur during the subsequent thermal breakdown. As observed in Fig. 5, the conversion value of the sample treated with acetic acid is about four times higher than that of the sample treated with sodium hydroxide at 320 °C.

The samples' reaction rates are plotted in Fig. 6. The CFRP samples that were pre-treated with different solutions each show a distinct reaction peak, demonstrating that solvolysis stage had influence on the process of matrix degradation during pyrolysis. For samples pre-treated in acetic acid, there were four distinct peaks for each derivative thermogravimetric curve, while samples pre-treated with sodium hydroxide and sulphuric acid, each had three reaction peaks. The most significant peaks were observed during the main stage. In contrast, only two minor peaks were found in stages 1 and 3, (i.e. the beginning of the composite degradation process). CFRP pre-treated with 0.1 M acetic acid, 0.1 M sodium hydroxide, and diluted sulphuric acid exhibited reaction rates of 0.128%/°C, 0.071%/°C, and 0.154%/°C, respectively, at the first peak. The main degradation process and the maximum reaction rates occurred within a temperature range of 290–410 °C. Only one reaction peak was observed at approximately 370 °C for each hydroxide and diluted sulphuric acid; however, two reaction peaks were observed for acetic acid at approximately 295 °C and 370 °C. In the case of acetic acid, these two peaks have a lower value than those observed for other solutions. This may be owing to the rapid reactivity of acetic acid-treated CFRP and the earlier generation of pyrolytic carbon at lower temperatures, which can halt matrix degradation and reduce the conversion rate by a factor of two. The last peak occurred during stage three with an approximate temperature of 690 °C.

The final reaction behaviour for those with pre-treatment is more stable. The creation of irregular pores in the pyrolytic carbon layer may be responsible for this unique behaviour. In terms of thermal degradation of untreated CFRP, the formation of pores on the matrix is random and cannot be predicted during the pyrolysis process. These pores may group to create fast temperature changes and energy absorption in a specific location. This fact results in variable decomposition rates of the matrix at different places in an untreated CFRP sample. However, chemical pre-treatment can minimise this negative influence.

Compared to the other two solutions, it is evident that the utilisation

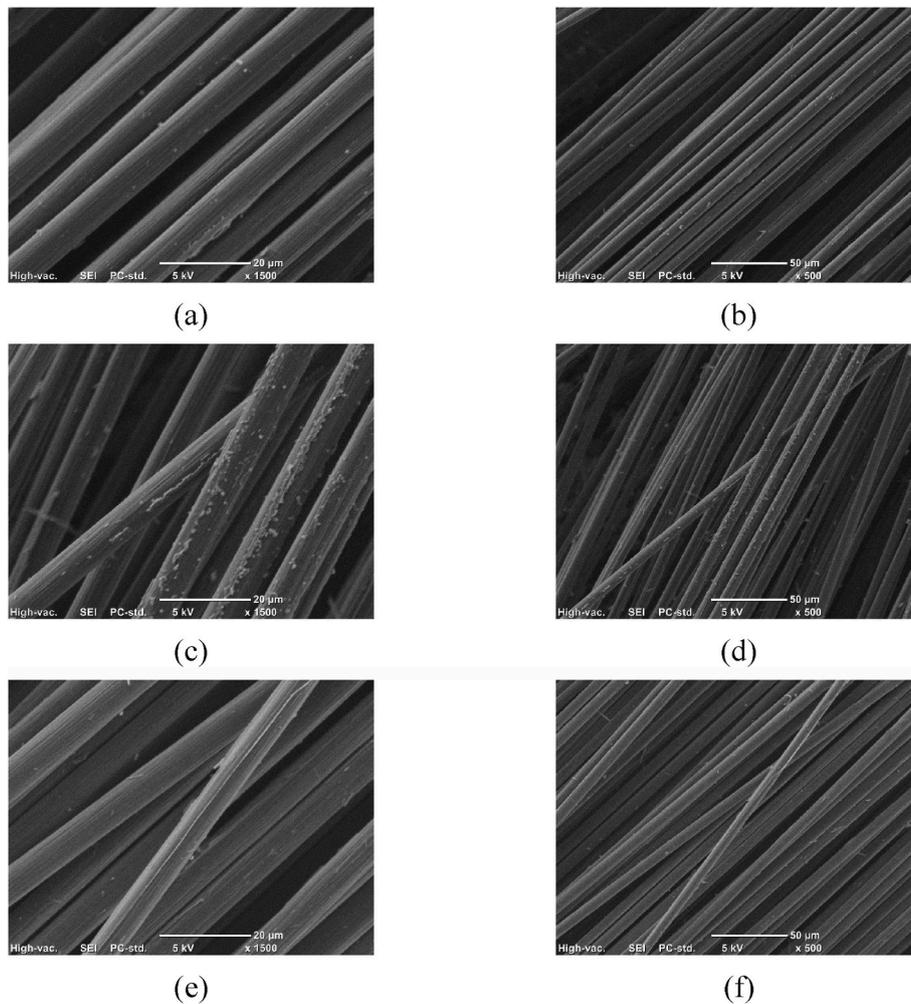


Fig. 7. SEM images of fibres recovered with pyrolysis and different pre-treatments: (a) and (b) acetic acid, (c) and (d) sodium hydroxide, (e) and (f) diluted sulphuric acid.

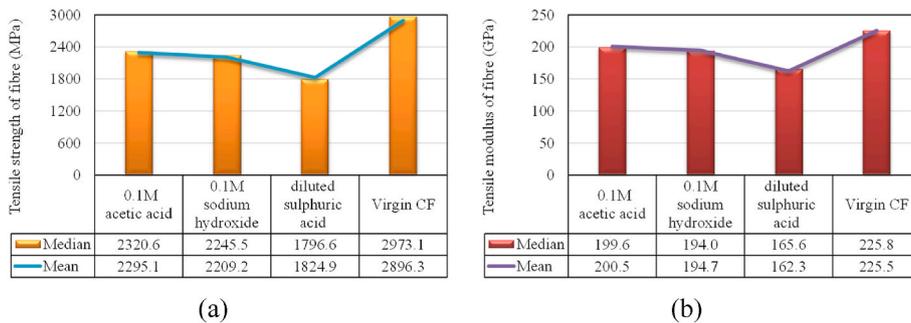


Fig. 8. (A) Tensile strength, and (b) tensile modulus of recovered fibres with different pre-treatments.

of acetic acid delivers cleaner recovered fibres (as shown in Fig. 7). There is only a limited amount of dot matrix on the surface of fibres recycled from CFRP that were pre-treated with acetic acid. In contrast, other fibres from the CFRP pre-treated with sodium hydroxide had an abundance of dot matrix and linear patterned matrix. The fibre in samples treated with diluted sulphuric acid were cleaner than the one treated with sodium hydroxide. However, a significant quantity of linear patterned matrix and char was still detected in SEM images. This may be because acetic acid helps to remove more matrix than the other two solutions before the thermal degradation process.

Ten tensile strength tests were carried out to evaluate the degree of

difference in tensile strength between recycled and virgin carbon fibres and the median and mean value of the results are shown in Fig. 8. Based on these results, it is evident that the combination of the pre-treatment and thermal degradation process leads to recycled carbon fibres with high tensile capacities. Virgin carbon fibre had an average tensile capacity of 2896.3 MPa. In contrast, the average tensile strength of recycled carbon fibre during pre-solvolysis with 0.1 M acetic acid, 0.1 M sodium hydroxide, and diluted sulphuric acid was 2295.1 MPa, 2209.2 MPa and 1824.9 MPa, respectively. This demonstrates that the strengths of the recycled fibres via three different process combined chemical pre-treatment and pyrolysis are 79%, 76% and 63% of that of its virgin state,

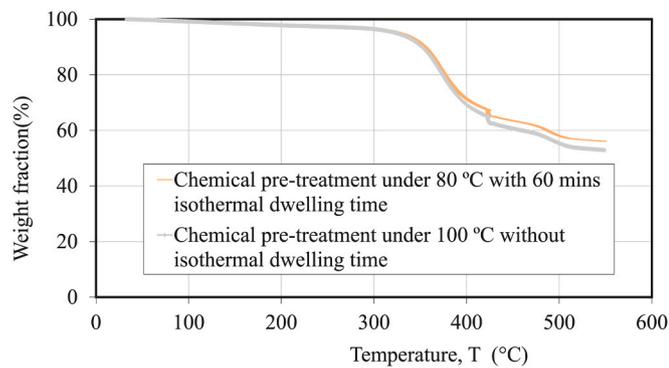


Fig. 9. Weight losses for composites with different pre-treatments during the optimised thermal degradation process (combination of effective pyrolysis and oxidation).

respectively. This results also suggest that, in these experiments, acetic acid is the most promising solution for solvolysis pre-treatment to achieve high-quality recycled fibres from CFRP wastes.

Based on the above kinetic behaviour studies, surface condition and mechanical properties examination of recovered fibres, it is observed that chemical pre-treatment can contribute to quick matrix dissolution at low temperature and produce high tensile strength fibres. However, following the pyrolysis process, some matrix was still left behind, and also the pre-treatments at ambient temperature contributed to the low productivity of the recycling process. Hence, it is advisable that the pre-treatment operation is carried out at the higher temperatures, as will be discussed in the subsequent section.

3.2. Effects of pre-treatment solution's temperature on CFRP decomposition

To maximise economic efficiency and increase productivity of recycling process, the duration of the pre-treatment procedure needs to be minimised. In this research, 80 °C with a 60-min isothermal dwelling and 100 °C without an isothermal dwelling were examined to reduce the recycling duration. The sample was properly dried after pre-treatment before testing in TGA. The optimised thermal recycling process established was utilised to remove matrix and obtain high-quality recovered fibres. This process combines effective pyrolysis up to 425 °C and secondary oxidation up to 550 °C with heating rate of 15 °C/min which was initial proposed by the authors in Ref. [24] and subsequently refined. After a certain period of time, the complete change of the atmosphere from nitrogen gas to air is made possible by a stage of equilibrium. In this experiment, kinetic analysis was performed to accurately assess the effects of various chemical pre-treatments on the degradation mechanism of composites. The Coat-Redfern model was used for calculation of the activation energy.

The data collected on the weight loss that took place throughout the process of CFRP degradation is provided in Fig. 9. This figure demonstrates that the overall thermal decomposition behaviour for two distinct solvolysis reactions is quite similar when subjected to pyrolysis. During the pyrolysis stage of the reaction, a more significant breakdown was observed, which resulted in a weight loss of around 35%. However, during the oxidation process, a greater portion of the matrix was eliminated from the CFRP that was pre-treated under 100 °C acetic acid without isothermal dwelling compared to the one that was pre-treated under 80 °C acetic acid with 60 min of isothermal dwelling. This demonstrates the impact of pre-treatment temperature on the behaviour of the following thermal recycling process. The treatment with a higher temperature without isothermal dwelling was more efficient in increasing epoxy breakdown while maintaining the same energy usage. At the end of the procedure, the relative weight losses for pre-treated samples at temperatures below 80 °C with 60 min of isothermal

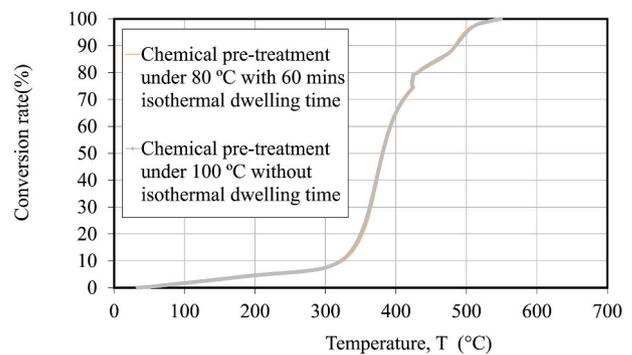


Fig. 10. Conversion rate of composites with different pre-treatments during the optimised thermal degradation process (combination of effective pyrolysis and oxidation).

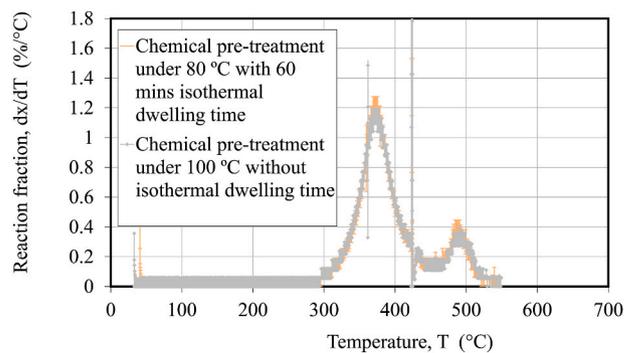


Fig. 11. Reaction fraction of composites with different pre-treatments during the optimised thermal degradation process (combination of effective pyrolysis and oxidation).

residence and below 100 °C without isothermal dwelling are, respectively, 53 and 56%.

Fig. 10 illustrates conversion rate of CFRP composites. This was developed based on the mass change of CFRP during the combined pyrolysis and oxidation process. According to the findings, the thermal deterioration of CFRP with pre-chemical treatment consists of five major stages: The first step, which lasts up to 300 °C and eliminates up to 7% of the epoxy matrix, is followed by a second stage that occurs between 300 and 425 °C. Stage 2 is the primary step of the pyrolysis reaction. For the transition from pyrolysis to oxidation to occur steadily, a 2-min reaction equilibrium phase was considered. The final two phases occur during secondary oxidation at temperatures ranging from 425 °C to 465 °C and from 465 °C to 550 °C to eliminate all residues and generate clean carbon fibres. The creation of pyrolytic carbon coated on fibre may lead to the formation of stage 4 and stage 5 of degradation process.

Fig. 11 is a graph generated after obtaining the reaction rates of the samples. The derivative thermogravimetric curve for both acetic acid treated specimens exhibited two unique peaks. The most substantial peak was observed during the primary stage of pyrolysis, whereas secondary recycling utilised oxidation to remove the leftover matrix and chars, resulting in a smaller reaction peak. The relative reaction rates at 367 °C and 490 °C were approximately 1.187%/°C and 0.412%/°C, respectively. Some scattered results were observed at around 425 °C that may reflect the unstable behaviour of the thermal degradation due to transitioning from an anaerobic degradation to an aerobic oxidation by changing of the inlet gas from nitrogen to oxygen. Based on these results, modest changes in the pre-treatment temperature have little influence on the conversion rate and reaction fraction.

Various kinetic analysis methods of the Arrhenius type have been developed by further altering equations and making various assumptions. There are two primary methods: model-fitting and model-free.

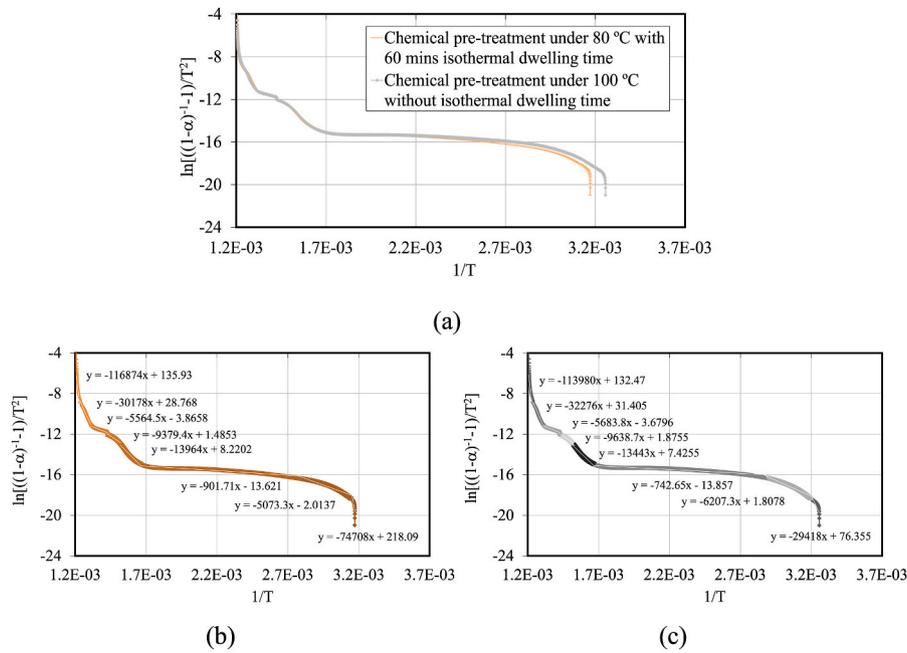


Fig. 12. $\ln(((1-\alpha)^{-1}-1)/T^2)$ versus $1/T$ for different pre-treatments (a) with eight regions divisions for temperatures up to (b) 80 °C with 60 min isothermal dwelling, (c) 100 °C without isothermal dwelling.

Comparing the advantages and disadvantages of different techniques reveals that one of the fundamental assumptions of model-free approaches lack precision, namely that fluctuations in the heating rate have no influence on kinetic performance. This assumption disregards the fact that the reaction is delayed as the heating rate increases during thermal degradation [24]. To accurately assess the kinetic behaviour during the thermal decomposition process, the activation energies required for the degradation process were calculated using the Coats-Redfern approach, which is one of the single-curve methods for establishing the mechanism of decomposition by employing the asymptotic assumption.

This approach is also known as the integral method or the twofold integration method since it is obtained by integrating Equation (4) twice, followed by calculating the Napierian logarithm, as illustrated in Equation (5) [27]. Equation (6) represents the Coats-Redfern technique’s formulation [26].

$$\frac{d\alpha}{dt} = kf(\alpha) = k(1 - \alpha)^n \tag{5}$$

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} (1 - \alpha)^n \tag{6}$$

where $g(\alpha)$ reflects the reaction model based on the thermal mechanism of the material.

The activation energy was computed using linear regression for $\ln[g(\alpha)/T^2]$ versus $1/T$ curves for each conversion rate. The slope of the curves are equal to $-E/R$; hence this allows the activation energy to be estimated. Fig. 12 depicts the $\ln(((1-\alpha)^{-1}-1)/T^2)$ value in comparison to the $1/T$ value for two distinct pre-treatments. Because the process of CFRP disintegration is complex and combines two distinct forms of thermal degradation (i.e. pyrolysis and oxidation), the Coats-Redfern approach cannot be utilised directly to analyse this process [28,29]. Consequently, the entire process is subdivided into smaller sections, each characterised by a straight line (see Fig. 12). The thermal degradation of CFRP was modelled using eight sections, with conversion fractions ranging from 0 to 10, 0.1 to 10, 1 to 10%, 10 to 50, 50 to 75, 75 to 90, and 90 to 99, 99 to 100%, respectively. This approach resulted in a linear study of trendlines for eight divided parts within a non-linear parabolic curve. The combination of these behaviours can describe the

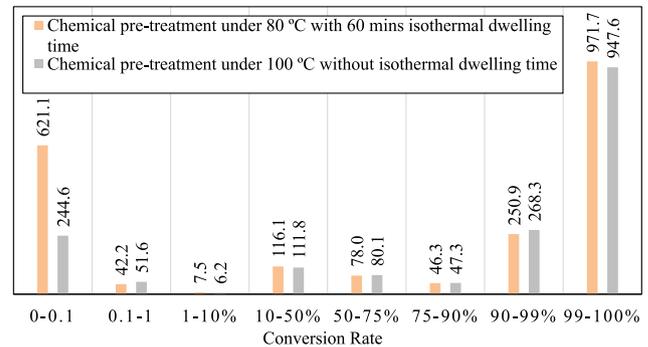


Fig. 13. Activation energies derived using Coats-Redfern method.

entire thermal deterioration of CFRP. Hence, it is now possible to study reaction mechanisms using the Coats-Redfern approach.

The activation energies corresponding to each section are presented in Fig. 13. This shows a considerable amount of energy is required to initiate the reaction under nitrogen. Upon removing 0.1% of the matrix, the activation energy reduces from 600 kJ/mol to around 50 kJ/mol and eventually decreases to less than 10 kJ/mol. The activation energies were lowest when the matrix conversion was between 1 and 10%. The subsequent increase in activation energy after 10% conversion indicates the beginning of the main reaction phase of CFRP thermal degradation during the pyrolysis process. The activation energy for the conversion between 10% and 75% is within the range of 78.0–116.1 kJ/mol. A low energy response value for a conversion fraction of 75–90% indicates that the pyrolysis process is complete and secondary oxidation has begun. After this stage, large activation energies are observed for the oxidation of the remaining matrix and pyrolytic carbon, particularly for the final 1% of conversion. According to the activation energy research results, pre-treatment at 100 °C with no isothermal dwelling time can perform better than pre-treatment at a lower temperature and longer isothermal stay time.

In terms of the surface morphology of recovered carbon fibres, the results of SEM tests reveal that clean carbon fibre could be obtained

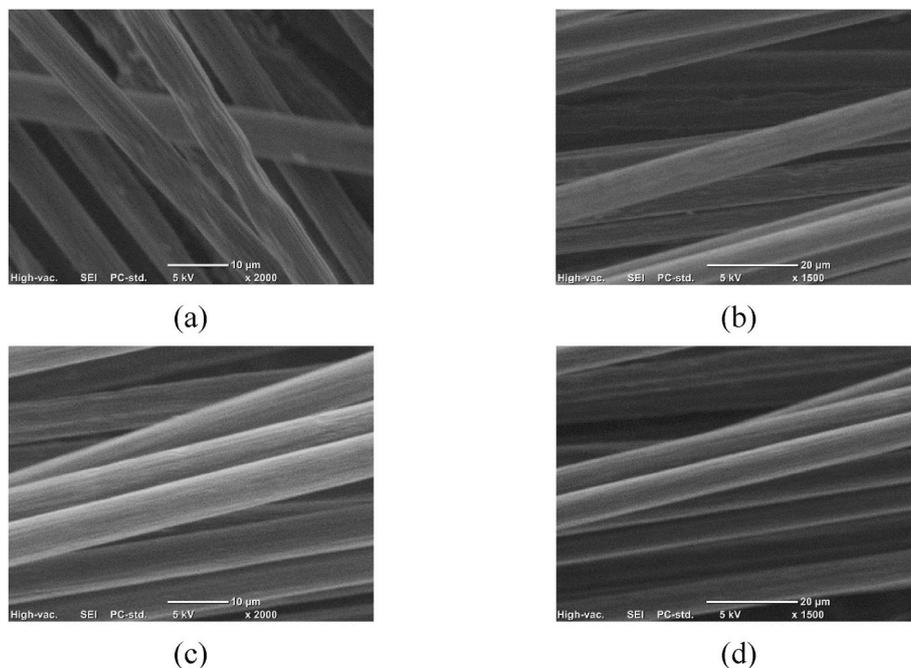


Fig. 14. SEM images of fibres recovered with different pre-treatments: (a) and (b) for heating up to 80 °C with 60 min isothermal dwelling, (c) and (d) for heating up to 100 °C without isothermal dwelling.

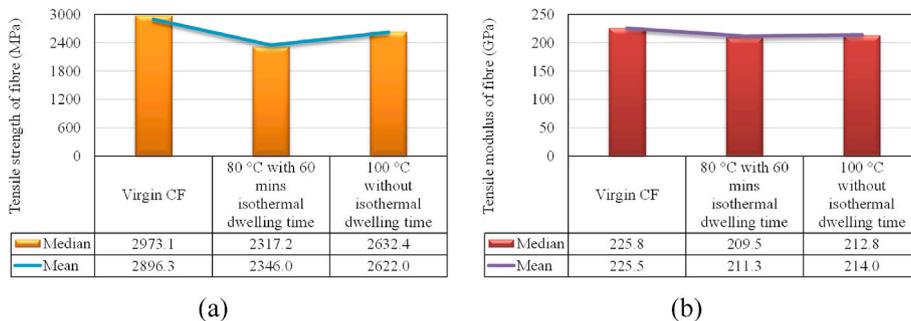


Fig. 15. (A) Tensile strength, and (b) tensile modulus of recovered fibres with different heating system involved during chemical pre-treatment.

without remaining matrix and char, as seen in Fig. 14. For the samples pre-treated at 80° Celsius with 60 min of isothermal dwelling, damages to the fibres were observed as it can be seen in Fig. 14(a). In contrast, fibres with higher quality and a smoother surface were produced by the pre-treatment at temperatures lower than 100° Celsius and without the use of an isothermal dwelling prior to pyrolysis process.

Fig. 15 summarises the findings of tensile tests conducted on fibres that were recovered after being treated with two different pre-treatments. Results demonstrate that recycled carbon fibres have a high tensile capacity even after solvolysis pre-treatment and pyrolysis and oxidation processes. It compares the outcomes of tensile strength tests between recycled and virgin carbon fibres. The median tensile strength and tensile modulus of virgin carbon fibre was 2973.1 MPa and 225.8 GPa, respectively. In contrast, the median tensile strength of recycled carbon fibre pre-treated at 80 °C with 60 min of isothermal dwelling and 100 °C without isothermal dwelling was 2317.2 MPa and 2632.4 MPa, respectively. By comparing the average tensile strength of recycled carbon fibres and virgin carbon fibres, results reveal that the strength of recycled fibre can be maintained to up to 90.5% of its virgin condition if appropriate pre-treatment is performed prior to thermal degradation. In terms of tensile modulus, the influence of pre-treatment solution temperature on CFRP decomposition is negligible, with a difference of just 1% (94% of virgin state for 80 °C with 60 min of

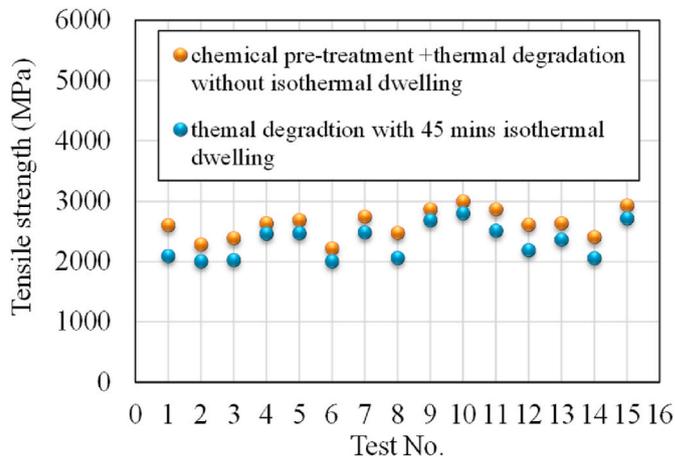


Fig. 16. The effect of chemical pre-treatment on tensile strength of recovered fibres.

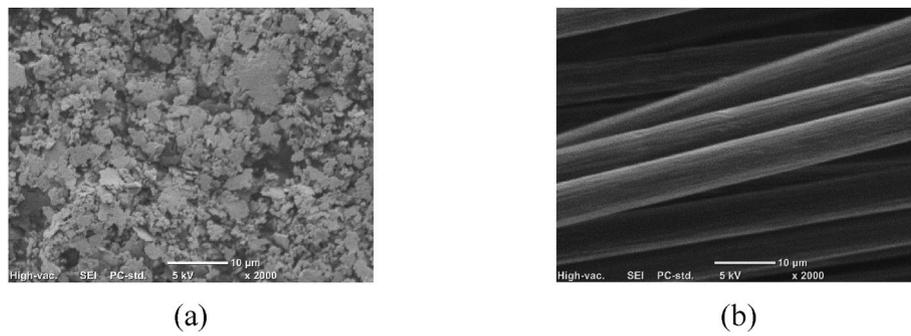


Fig. 17. SEM Images for (a) CFRP after chemical pre-treatment and (b) fibre recovered with optimised thermo-chemical recycling technique.

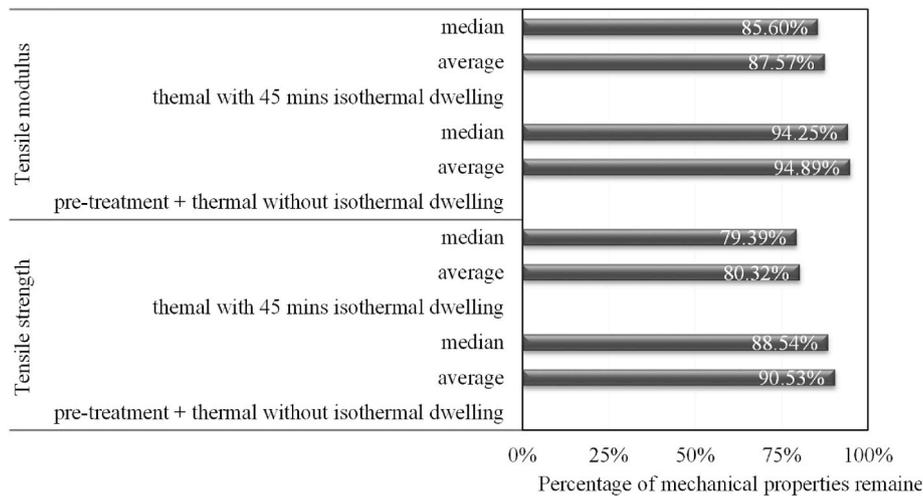


Fig. 18. Properties of fibres recovered from CFRP via thermal only and hybrid thermo-chemical technique.

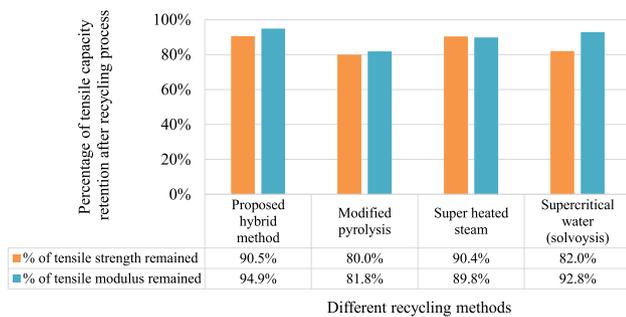


Fig. 19. Comparison between different recycling methods [30–32].

isothermal residence and 95% of virgin state for 100 °C without isothermal dwelling).

As depicted in Figs. 16 and 17, the application of an adequate chemical pre-treatment prior to the thermal degradation process not only helps to reduce energy input by minimising the isothermal residence time, but also results in clean fibres with greater tensile strength. Fig. 18 compares the mechanical properties of fibres recovered from CFRP via two developed techniques. It reveals that the recycled fibres can retain up to 90.53% of their virgin strength, which is 10.21% higher than the strength of recycled fibres that have not been pre-treated with solution. Fig. 19 illustrates the comparison of tensile capacity retention between the proposed method and the thermal and chemical recycling methods already existing in the literature. On the basis of these findings, the suggested recycling technique comprises 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.

3.3. Recycling of a decommissioned bike fork and airplane scraps

It has been reported that the aerospace and sporting goods industries have a significant consumption of CFRP composites with level reaching 23–26% and 13–15%, respectively [33]. As a result, a considerable amount of waste is generated in these industries. Furthermore, the aviation industry is expected to accumulate a staggering amount of 500, 000 tonnes of CFRP end-of-life and manufacturing scraps by 2050 [34]. Hence, the practical viability of the proposed hybrid thermo-chemical recycling method was evaluated by recycling the fork of a commercial bicycle and scraps from an aeroplane made of CFRP composites, as illustrated in Fig. 20. The bicycle fork studied in this research was fabricated from high-strength unidirectional carbon fibre mats coated with a sealant. The recycling of these bicycle forks allowed us to study the effect of the coating on the efficiency of the recycling procedure, including how the coating removal process may affect the chemical and thermal degradation of the matrix and the mechanical properties of recovered fibres. The airplane scraps were made of bi-directional carbon fibre mats with no additional coating.

Fig. 21 demonstrates that, fibre recovered from polished waste (i.e. removing the coating with a fine sanding machine) has a cleaner surface than fibre recovered directly from decommissioned bike. In terms of coating's impacts on mechanical properties, the tensile strength and modulus of recycled carbon fibre from bike waste that was polished with a fine sander were evaluated and compared to those of fibre recovered from untreated bike waste. Multiple tests were conducted to assess the variation in tensile capacity; the average tensile capacity of various

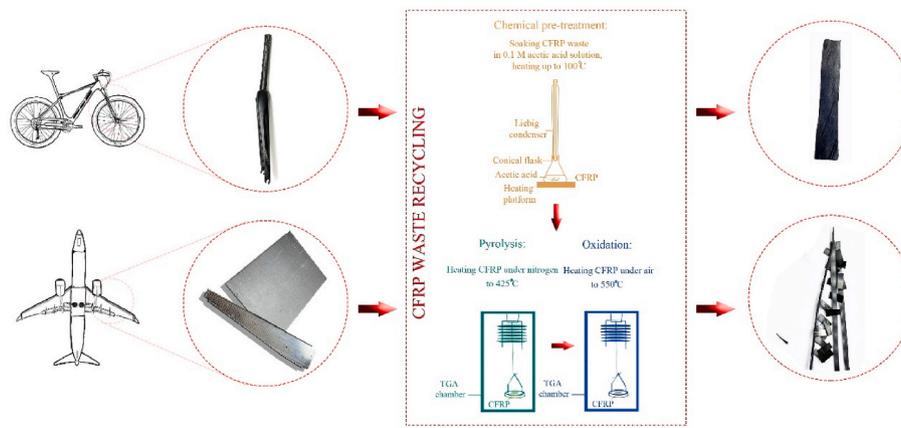


Fig. 20. Recycling of bike fork and airplane scraps.

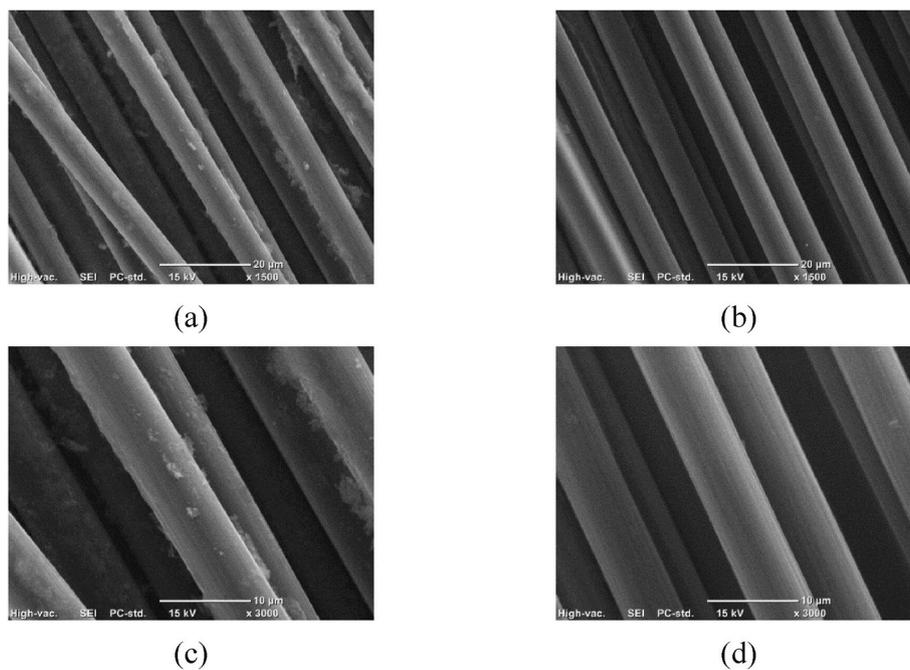


Fig. 21. Recovered carbon fibre from (a) and (c) bike fork with coating and (b) and (d) bike fork without coating (coating removed via fine graded polishing) prior to recycling process.

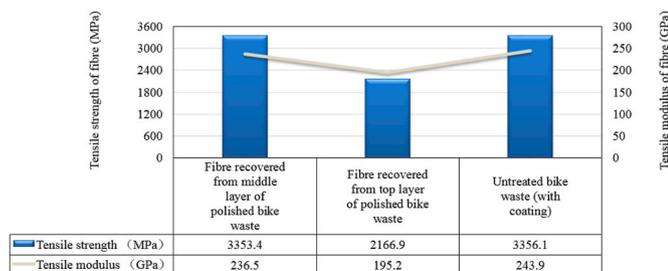


Fig. 22. Average tensile strength and tensile modulus of different recycled fibres.

recycled fibre types is depicted in Fig. 22. There is no significant difference in tensile strength between fibres recovered from untreated bike waste and fibres recovered from the middle layer of polished waste. However, the tensile strength of fibre recovered from the top layer of polished bike is approximately 1190 MPa lower than the other two,

indicating that 35.4% of the fibre’s strength could be lost during the sanding procedure. In terms of material stiffness, the recycled carbon fibre from polished bike waste showed a slightly lower tensile modulus than untreated waste at 236.5 GPa. This disparity in values between the top and middle layers indicates that the sanding procedure caused significant damage to the fibre, as 17.5% of its tensile modulus was reduced after polishing.

To discover the effect of chemical pre-treatment on thermal degradation, properties of fibres recycled via thermal only and hybrid thermo-chemical recycling were compared. As shown in Fig. 23, the average tensile strength and modulus of carbon fibres recovered through thermo-chemical recycling were 7% and 5% greater than thermal recycling, respectively. Also, scanning electron microscope (SEM) results demonstrate that in terms of surface topography, fibre recovered from hybrid method has a cleaner surface than fibre recovered via thermal degradation without isothermal dwelling time or chemical-pre-treatment. This study also demonstrates that there is no significant difference in tensile strength between fibres recovered from untreated bicycle waste and fibres recovered from the middle layer of polished waste. However, SEM

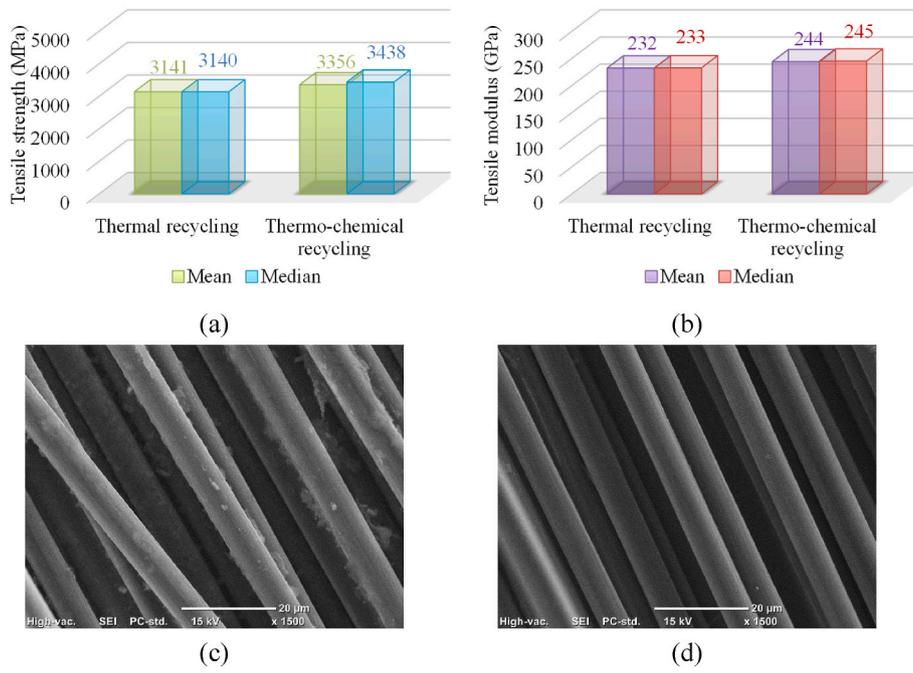


Fig. 23. Comparison of tensile strength (a), modulus (b) and surface properties (c)&(d) of recycled carbon fibres via different techniques. Note: SEM images for the fibre recovered via thermal only and hybrid system are (c) and (d), respectively.

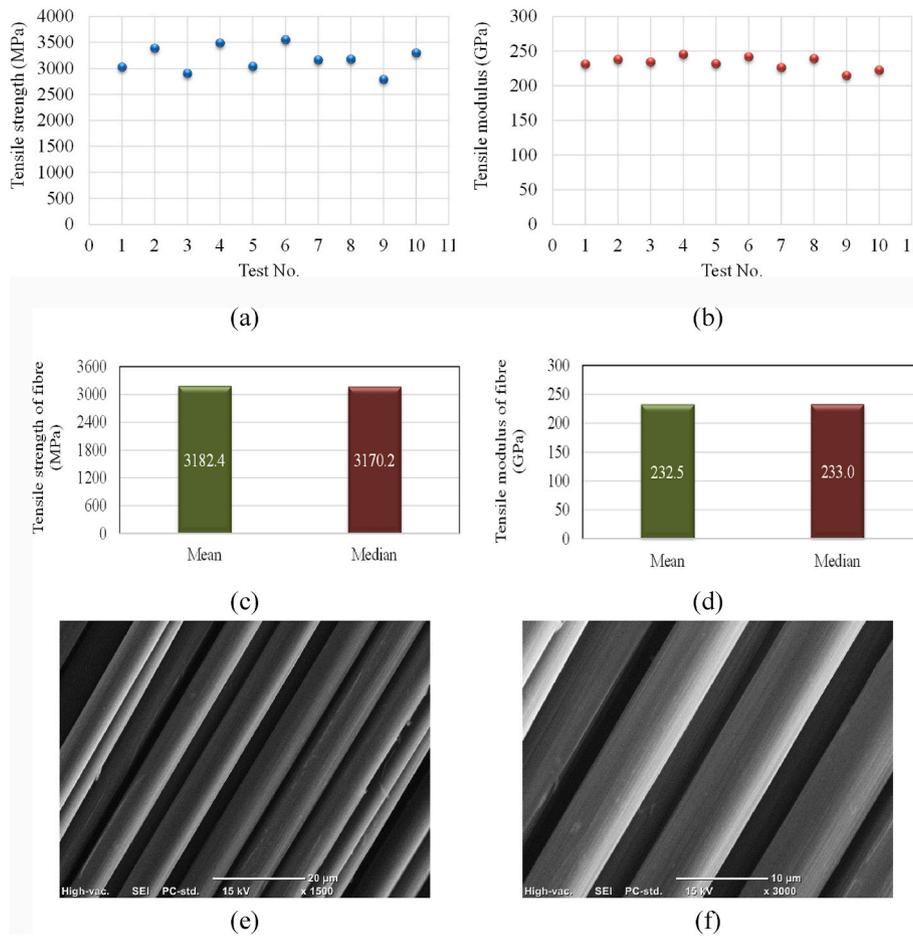


Fig. 24. Tensile strength (a and c) and modulus (b and d) of recovered fibres from airplane wastes, and (e and f) SEM images with magnification of (e) \times 1500 and (f) \times 3000.

experiments revealed that fibre recovered from polished waste has a cleaner surface than fibre recovered directly from a decommissioned bicycle. These findings reveal the effectiveness of coating removal and chemical pretreatment processes.

This process was also used to recycle the aircraft's scraps from internal mezzanine layer, which is without coating. As indicated in Fig. 24, the average tensile modulus and tensile strength of recovered carbon fibres were 232.5 GPa and 3182.4 MPa, respectively. To further investigate the surface qualities of recycled fibres, the cleanliness and surface deterioration of the fibres were assessed. Fig. 24 demonstrates that there is a negligible quantity of matrix residue on the fibres, which is marginally higher than that of the bike samples. Based on the nature of the matrix, this may indicate that the parameter needs to be modified somewhat for different forms of CFRP.

4. Conclusions

In this study, an optimised chemical pre-treatment method was developed, which can be employed prior to thermal degradation procedure by taking into account the solution selection and heating mechanism. The pre-treatments at room temperature were carried out using three different solutions, including diluted sulphuric acid (20% wt H₂SO₄), weak acetic acid (0.1 N CH₃COOH), and weak sodium hydroxide (0.1 N NaOH). The results of TGA showed that the pyrolysis process of chemically pre-treated CFRP is comprised of three primary stages: step one which lasts up to 180 °C and eliminates 10% of the epoxy matrix, and stage two which can be considered as the primary reaction stage occurs between 180 °C and 425 °C. The final stage takes place at 425 °C–700 °C to remove the remaining 15% matrix and chars. In contrast to untreated CFRP, which only contains two reaction stages, pre-treated CFRP has an additional preliminary reaction step, allowing for a higher level of breakdown at lower temperatures. At the same temperature, acetic acid causes more primary debonding in the material's inter structure due to two reasons: First, acetic acid-treated samples have a greater conversion value. For instance, the value is approximately four times that of the sample treated with sodium hydroxide at 320 °C. Second, hydroxide and diluted sulphuric acid each had one reaction peak at 370 °C, whereas acetic acid had two at 295 °C and 370 °C to allow further reaction at the preliminary stage. Regarding the quality of recycled fibres, it is evident that the use of acetic acid provides cleaner fibres with higher tensile strength.

In order to maximise economic efficiency and enhance productivity, it is necessary to reduce the processing time of the pre-treatment technique examined at the primary stage. For this, 80 °C with an isothermal residence of 60 min and 100 °C with no isothermal residence were studied as potential heating strategies of solvolysis to accelerate reaction process. To effectively remove the matrix and obtain high-quality recovered fibres, the optimised thermal recycling process outlined in our previous study was used. TGA tests indicated that treatment with 100 °C without isothermal dwelling is able to effectively enhance epoxy degradation while retaining the same energy consumption. The kinetic behaviour analysis also demonstrated that the pre-treatment at 100 °C with no isothermal dwell time required lower activation energies than the one with 80 °C with an isothermal residence of 60 min. In terms of the surface morphology of recycled fibres, pre-solvolysis at 100 °C can yield fibres with higher quality and a smoother surface. The strength of these recycled fibres can be preserved to up to 90.53% of their virgin condition, which is significantly higher than the strength of recycled fibres that have not been pre-treated (80.32%).

In terms of energy consumption behaviour, the activation energy decreases from 600 kJ/mol to 50 kJ/mol, and subsequently to 10 kJ/mol when only 0.1% of the matrix remains. The activation energy shows a decreasing trend when the matrix is reduced by between 1 and 10%. However, after 10% conversion, the activation energy increases, indicating the initiation of CFRP thermal breakdown during pyrolysis. For a conversion rate of 10%–75%, the activation energy falls within the

range of 78.0–116.1 kJ/mol. When the energy response value is small for a conversion percentage of 75%–90%, it suggests that pyrolysis is complete and secondary oxidation has begun. High activation energies are observed in the final 1% of conversion, particularly in matrix and pyrolytic carbon oxidation. Activation energy studies showed that pre-treatment at 100 °C with no isothermal dwell time outperforms pre-treatment at lower temperature and longer dwell time.

Based on these results, 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. 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.

Credit author statement

Yaning Wei: Data curation; Formal analysis; Investigation; Software; Validation; Methodology; Visualisation; Writing – Original Draft.

Ali Hadigheh: Conceptualisation; Data curation; Funding acquisition; Investigation; Methodology; Project administration; Resources; Supervision; Validation; Writing – Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

This research was supported by the Australian Government through the Australian Research Council's Discovery Early Career Researcher Award (DECRA) fellowship scheme (project DE200100406) which was received by the second author. Authors would like to thank the School of Civil Engineering at the University of Sydney for supporting this project and Cycle Inspect for providing bike fork. Authors would also like to acknowledge the Sydney Microscopy & Microanalysis for providing access to the scanning electron microscope.

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