Recycling of Carbon Fibre via Pyrolysis Technologies

By

Siqi HAO

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Abstract

Carbon fibre reinforced plastic (CFRP) composites have been widely used in many industrial fields, such as the automotive and aviation industries, due to their impressive properties including being lightweight, corrosion-resistant and having a high strength to weight ratio. This inevitably generates large amounts of composites waste during the manufacturing process and when these composite products reach the end of their service life. Considering the environmental and economic impact, composites recycling has become one of the top priorities for composite industries. Currently the main recycling techniques that have been developed include mechanical recycling, chemical solvolysis and pyrolysis. Among all these, pyrolysis has been proven to be the most promising recycling technique. This study focuses on pyrolysis techniques, further optimizes and develops pyrolysis methods including conventional pyrolysis, hybrid pyrolysis method and microwave pyrolysis from the aspect of char elimination, so that a higher quality carbon fibre can be recovered with a potential for energy saving.

At the beginning of the study, an optimization of conventional pyrolysis was conducted to reduce the char formation via the thermal analysis of two types carbon fibre thermoset composite. The effect of pyrolytic conditions, in terms of heating rate, pyrolysis temperature and inert gas flow rate on char retention and intrinsic reactivity were investigated. It was found the pyrolytic char formation reduced as the heating rate, pyrolysis temperature, and gas flow rate increased, whilst the char intrinsic reactivity increased with fast heating rate and low temperature. The improvement in intrinsic reactivities were attributed to the rise in oxygen-to-carbon ratio, char pore size, and BET surface area. A more porous structure was observed from the char generated from a fast heating rate and high temperature. This consolidated the effect of pyrolytic conditions on the char intrinsic reactivity. This research confirmed that the appropriate selection of pyrolytic reaction conditions not only reduces the char yield, but also improves the char oxidation activity.

Secondly, a new hybrid recycling approach was developed to reduce char formation significantly using a combination of a chemical pre-treatment followed by a conventional pyrolysis process. Zinc chloride/ethanol solution was selected as the pre-treatment agent. After immersing carbon fibre epoxy prepreg in the 40 wt.% $ZnCl_2/C_2H_5OH$ solution at 80 °C for 2 hours, some tiny cracks appeared on the surface of the prepreg and the required pyrolysis temperature reduced. The surface morphology and chemistry, mechanical performance of recycled carbon fibre have been investigated. The recycled carbon fibres retained a competitive mechanical performance closed to virgin carbon fibre and appeared to have a relatively clean surface with small residues. As compared with the standard pyrolysis recycling process, this hybrid method results in carbon fibre with higher mechanical performance.

Finally, the utilisation of microwave pyrolysis was attempted in a multi-mode microwave reactor to potentially improve the pyrolysis efficiency. The pyrolytic products distributions and properties of carbon fibre epoxy prepreg pyrolyzed at different microwave temperatures of 450 °C, 550 °C and 650 °C were investigated. It was found that higher temperatures resulted in less char formation and a higher yield of gas and liquid products. The carbon fibre recovered at 450 °C showed the highest tensile strength, while there was no significant change in tensile modulus for carbon fibre extracted at different microwave temperatures. The recycled carbon fibre showed a relatively clean surface, with increasing number of oxygen-containing groups. The gas released from the process has a composition of H_2, CO and CO_2, and the major liquid product components are phenols and aromatics. The microwave pyrolysis has demonstrated a potential as a low energy consuming method of carbon fibre pyrolysis recycling.

In summary, carbon fibre was successfully recycled from a carbon fibre composite using various pyrolysis technologies in this research. The optimization and development of these pyrolysis technologies have the potential not only to reduce or eliminate the char formation, but also to recover high-quality fibre and save thermal energy.

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Achievements

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Xiaoling Liu, **Siqi Hao**, Chapter 5. Composite recycling via microwave technologies *Composite recycling and reuse*. (2020) (in editing)

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List of Abbreviations

BET area	Brunauer–Emmett–Teller area
BT	Burnout temperature
BPF	Bisphenol F type epoxy resin
CF	Carbon fibre
CF/EP	Caron fibre reinforced epoxy
CF/PF	Caron fibre reinforced phenolic
CFRP	Carbon fibre reinforced plastic
D bond	Disordered band of Raman
DDM	Diamino diphenylmethane
DTG	The first derivative of the mass loss curve
EDS	Energy dispersive X-ray spectrometer
EOL	End-of-life
EP	Epoxy
EU	European union
FWHM	The full widths at half maximum
FB	Fluidised bed process
FID	Flame ionization detector
G band	Graphitic band of Raman
GC	Gas chromatography

GC-MS	Gas chromatograph mass spectrometry
GFRP	Glass fibre reinforced plastic
O/C	Oxygen to carbon ratio
SCF	Supercritical fluid
SE2	Secondary electron detector
PF	Phenolic
PE	Polyethylene
PES	Polyester
PP	Polypropylene
PT	Peak temperature
PVC	Polyvinyl chloride
PET	Polyethene terephthalate
rCF	Recycled carbon fibre
vCF	Virgin carbon fibre
SEM	Scanning electron microscopy
SFTT	Single fibre tensile test
TCD	Thermal conductivity detector
TPA	Terephthalic acid
TGA	Thermogravimetric analyser
TG	Mass loss curve

UPR	Unsaturated polyester resin
XPS	X-ray photoelectron spectroscopy

List of symbols

°C	Degree Celsius
%	Percentage
wt.%	Weight percentage
vol.%	Volumetric percentage
at.%	Atomic percentage
s	second
min	Minute
h	Hour
µm	Micron
mm	millimeter
cm	centimeter
m	meter
ml	milliliter
cm^3	Cubic centimeter
m^2	meter square
m^3	Cubic meter
K	Kelvin
eV	electron volt
V	Volt

kV	kilovolt
W	Watt
kW	kilowatt
M	Mole
g	Gram
kg	kilogram
cal	Calorie
MJ	Mega joule
N	Newton
MPa	Megapascal
GPa	Gigapascal
ID	Intensity of D band
IG	Intensity of G band
rpm	rev per minute

Chapter 1. Introduction

1.1. Research background

Carbon fibre reinforced plastic (CFRP) composites have been widely used in automotive, aerospace, transportation, and many other industrial fields due to their unique combination of low-weight, high elasticity modulus, and high strength properties in comparison with traditional metallic materials (Yu et al., 2016). A large proportion of CFRPs are manufactured using thermoset resin for its high thermal stability, good mechanical performance, and low cost. The high specific performance serves as the driving force behind CFRP's domination of the composite markets as it meets consumer demands (Sloan, 2016). However, it poses a great threat to the environment at the end of its service life. The quantities of carbon fibre production waste and end-of-life waste are estimated to be 62 000 tonnes by 2020 (Meng et al., 2018). Industries face a significant challenge in recycling these composites, mainly due to the irreversible cross-linked structure of the thermoset matrix. To deal with the ever-increasing end-of-life parts and manufacturing wastes, a variety of recycling technologies, such as chemical solvolysis, a fluidised bed process, and pyrolysis have been studied intensely across the globe (Pickering, 2006). Among the mentioned technologies, pyrolysis is the most preferable option due to its relatively low energy consumption and high retention of mechanical properties of the carbon fibre recycled from this technology (Wong et al., 2017; Yang et al., 2015). Also, pyrolysis is being practised by established companies, such as ELG Carbon Fibre Ltd, UK and Carbon Conversions Inc, US.

Pyrolysis treats composite waste at the temperature around 450-700 °C, in an inert environment to convert the thermoset matrix into volatile matters (pyrolytic gas and oil) and pyrolytic char (Marsh, 2008). The Figure 1-1 shows an example diagram of the carbon fibre composite, in which the resin matrix can be pyrolyzed and the carbon fibres remain unchanged and can be recycled after pyrolyzing. The volatiles can potentially be further processed for energy recovery or used as a feedstock for the manufacturing of lower molecular weight chemicals (Cunliffe and Williams, 2003b). The pyrolytic char, however, remains on the surface of the recovered carbon fibres, affecting the adhesion of recycled fibre with the matrix and impairing their reuse options. An extra oxidation or gasification process, using oxidizing gas at high temperature, typically 500-600 °C and taking about 20-60 minutes (Meyer et al., 2007; Yang et al., 2015), is necessary for char elimination to obtain clean carbon fibre. However, it has been noted that the mechanical performance of the recovered carbon fibre is greatly affected by undergoing the same oxidation or gasification process (Yang et al., 2015). Moreover, this extra char elimination process increases the total energy cost. Therefore, considering the energy cost and mechanical performance of recycled carbon fibre, the elimination of pyrolytic char is a big challenge in the pyrolysis process.

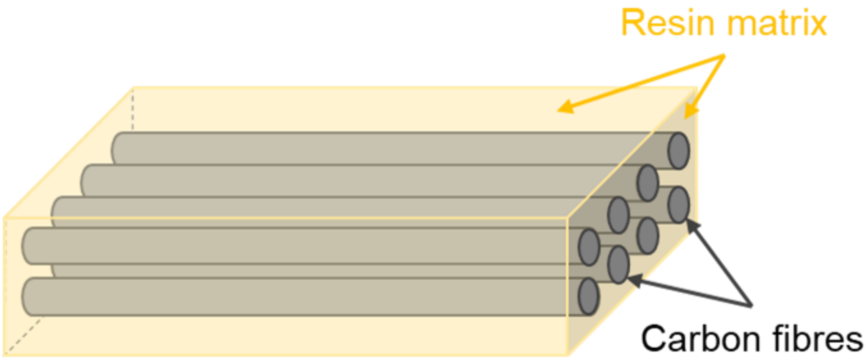


Figure 1-1 The example diagram of the carbon fibre composite.

Conventional pyrolysis has been widely used in industry and it has been the most appealing option for recycling CFRP waste (Job, 2014). Previous research on conventional pyrolysis of carbon fibre composite is rare and mainly focused on the feasibility of using this technology in recycling the CFRP waste using a single set of process conditions. The conventional pyrolysis process has not been well optimized to reduce undesirable by-products, such as pyrolytic char, or to recover the best products, while consuming the least energy. Thus, the pyrolysis process is still far from optimized.

Despite conventional pyrolysis being a common thermal treatment in many engineering applications, there remain a number of permanent drawbacks to this technology, i.e. low heat transfer efficiency, long heating duration, heat loss, and high energy consumption. Microwave heating, which is gradually being utilized in material processing, allows dielectric materials to interact with the microwaves and transform the electromagnetic energy into heat (El Khaled et al., 2018). The target material is volumetrically heated so that the heat transfer rate is relatively high. Microwave pyrolysis of carbon fibre composite has gained increasing interest due to its selective and rapid heating by microwaves (Clark and Sutton, 2003), potentially saving processing time and enabling energy savings (Emmerich and Kuppinger, 2014; Ulven et al., 2014). A survey of the literature reveals little research on the recycling of carbon fibre using microwave pyrolysis, and most studies implemented microwave pyrolysis at a single set of experimental conditions. Thus, there is a lack of systematic analysis of the recycling of carbon fibres using different microwave pyrolysis variables and the potential value of its pyrolytic product.

Therefore, this research focuses on the optimization and development of different pyrolysis technologies for the recovery of high-quality carbon fibre. Firstly, the optimization of conventional pyrolysis is considered. Then, a new hybrid approach which consists of a chemical pre-treatment process and conventional pyrolysis is proposed and developed. Finally, the microwave pyrolysis is attempted.

1.2. Aim and objectives:

The aim of this research is to optimize and develop different pyrolysis technologies in the drive to reduce or eliminate char formation for the recovery of high-quality carbon fibre. The specific objectives are as follows:

- To investigate the optimum convectional pyrolysis to achieve the minimum pyrolytic char formation. The effect of temperatures, heating rates, and gas flow rates on char formation of carbon fibre reinforced epoxy and phenolic prepreg are studied. The pyrolytic char derived from epoxy and phenolic resin is characterized using intrinsic analysis, elemental analysis, BET surface area test, and surface morphology analysis to study its oxidation behaviours.
- To propose and develop a new hybrid recycling approach which starts with a chemical pre-treatment process followed by

conventional pyrolysis, to reduce the char formation and recover clean carbon fibre straight from the conventional pyrolysis without the extra oxidations. The effectiveness of chemical pre-treatment on the degradation behaviour of carbon fibre reinforced epoxy prepreg is investigated. The quality of recycled carbon fibre is evaluated in terms of mechanical properties, internal structure, surface element, and surface appearance.

- To attempt the possible method of using a microwave pyrolysis process to recover the carbon fibre and potentially save thermal energy. The effect of different microwave pyrolysis temperatures on the properties of recycled carbon fibre are investigated in the field of mechanical performance, surface element, and appearance. The components and compositions of pyrolytic oil and gas are analysed.

1.3. Thesis structure

A total seven chapters are included in this thesis.

Chapter 1 covers the overall background, aim, and objectives of this research together with the structure of the thesis.

Chapter 2 introduces the use of carbon fibre composite and the challenges to its recycling. It reviews the conventional and emerging carbon fibre recycling technologies. The conventional pyrolysis and microwave pyrolysis are reviewed in terms of various pyrolysis conditions and pyrolytic products.

Chapter 3 elaborates all materials, chemicals, and methodologies. The latter consist of conventional pyrolysis, the hybrid approach, and microwave pyrolysis. Details are provided for the characterisations of the products including recycled carbon fibres, pyrolytic char, pyrolytic oil, and gas.

Chapter 4 concentrates on the conventional pyrolysis of two thermoset carbon fibre prepregs at various pyrolysis conditions together with analysis of their char oxidation behaviours in terms of intrinsic properties, element compositions, morphologies, and specific surface area.

Chapter 5 investigates a new hybrid recycling approach to recycle carbon fibre which starts with a chemical pre-treatment and is followed by conventional pyrolysis. The effects of chemical pre-treatment on prepreg and recycled carbon fibre are studied. The properties of recycled carbon fibre are characterized, and results are compared to that of fibre recycled from a standard pyrolysis recycling method.

Chapter 6 focuses on microwave pyrolysis to recycle carbon fibre at different temperatures, i.e., 450 °C, 550 °C and 650 °C. The analysis of thermal behaviours of prepreg and characterizations of recycled carbon fibre, pyrolytic oil and gas are covered.

Chapter 7 concludes the novelty points and the overall findings of this research and suggests possible avenues for the future study.

Chapter 2. Literature review

2.1. Introduction

Carbon fibre reinforced plastic (CFRP) composites are replacing some metallic components in the automobile, aerospace, weaponry, and other industries. The increased use of this material produces large amounts of manufacturing waste and end-of-life (EOL) components. Due to the energy intensive manufacturing process, carbon fibre is a high-cost and high-value material. Meanwhile, environmental regulations are more and more restrictive in terms of the degradation and disposal of composite material in landfill. Therefore, the recycling of carbon fibre has become an urgent issue in the composite industry and many researchers have proposed various solutions for recycling carbon fibre in the last two decades. In this chapter, the use of CFRP and the challenges to recycling it are introduced. Then, various composite recycling technologies are reviewed with the main attention on conventional and microwave pyrolysis recycling technologies.

2.2. Use of CFRP composite and challenges in recycling

Compared with traditional metallic material and other fibre reinforced composites, CFRP composites combine unique advantages of low-weight, high elasticity modulus, and strength (Yu et al., 2016). Principally, CFRP composite offers a 30% weight reduction over aluminium alloy. Such a weight saving contributes greatly to a range of industries, including automobile, aerospace, and weaponry, in terms of cost and energy consumption (Marsh, 2008). However, the increasing application of CFRPs has been generating an increasing amount of carbon fibre waste comprising end-of-life (EOL) prepregs, manufacturing offcuts, testing materials, and a large number of end-of-life components. Due to the limitations of the service lifespan in the first-generation carbon fibre composite aircraft, the disposal of a large amount of end-of-life waste will become a serious issue in the next several decades. For example, it is reported that 50 wt.% of Boeing’s 787 and Airbus A350 passenger airliners are made up of carbon fibre composite (Pickering, 2009), and by 2030 around 6,000 – 8, 000 commercial planes are scheduled to reach the end of their service years (Ye et al., 2013). Furthermore, abundant wastes have been generated during the composite production process, such as expired carbon fibre prepreg, offcut, and defective products. The EU Directive on Landfill of Waste (99/31/EC) classified CFRP as chemical waste, this led to high disposal costs in their post-treatment (European Commission, 1999). Furthermore, composite manufacturers in Europe are required to dispose of the wastes they produce in their move towards environmental impact elimination and cost saving (Rybicka et al., 2016). Additionally, the construction wastes also attributed largely among the CFRP waste due to CFRP’s good performance in structural strengthening. Many concrete beams and slabs have added CFRP into the tensile face to achieve greater strength with a lower weight (Lambert et al., 2015). The demand for carbon composite in the construction sector was estimated to be 2 300 tonnes in 2013 with an annual growth rate of 6% (Lambert et al., 2015).

Currently, the world produces an estimated 25,000 – 30,000 tonnes of carbon fibre each year (Marsh, 2008) and the annual demand for carbon fibre composite will be in excess of 140,000 tonnes in 2020 (Wang et al., 2019a). The global demand for carbon fibre is estimated to reach 117,000 tons and 194,000 tons for carbon fibre composite in 2022 (Zhang et al., 2020).

The polymeric composites need hundreds of years to decompose in landfill and could release toxic substances (Jiang et al., 2015), particularly the irreversible thermosetting polymer matrix, such as epoxy and phenolic resin. Compared with thermally reversible thermoplastic and metallic counterparts, the 3D cross-linking molecular structure of a thermoset matrix imposes a significant technological challenge on recycling. However, due to the good mechanical properties of carbon fibre reinforced thermoset composites, the extensive use of such materials could be maintained in a series of industrial applications in the near future (Sloan, 2016). In addition, energy-intensive manufacturing results in high energy cost, not to mention the high price of virgin carbon fibres (Altay et al., 2017). It has been forecast that demand for the new carbon fibre composites will continue to increase in the future, thus, out of consideration of the environmental impact and the economy, and sustainability of the CFRP industry, it is important to break with the disposal habit and recycle waste efficiently (Liu et al., 2004).

2.3. Conventional recycling technologies

Many technologies for recycling carbon fibre have been proposed and developed in the past several decades. Commonly, the conventional recycling technologies can be classified as mechanical recycling, chemical recycling, fluidised bed (FB) processing, and pyrolysis processing (Pickering, 2006). Among those technologies, mechanical recycling is the earliest; it aims to reduce the size of the waste composite. In chemical recycling, solvents such as nitric acid, alkali, and supercritical fluids, are mainly utilised to dissolve the polymer matrix. The fluidised bed (FB) process recovers fibre in a bed of sand particles being fluidised by large streams of hot air. The pyrolysis process is the most widely used technology and removes the polymer matrix by heating it in the absence of air at high temperature. The details of all methods are reviewed in the following sections.

2.3.1. Mechanical recycling

Mechanical recycling of composites has been evidenced since the 1990s. Most research has focused on the granulation of waste thermoset composite and adopted the fine powder as a replacement for the filler, especially for glass fibre reinforced plastic (GFRP) composite. Mechanical recycling of CFRPs and GFRPs mainly involves mechanical comminution by cutting, grinding, and milling to reduce the size of the waste composite (Oliveux et al., 2015; Pickering, 2006; Pimenta and Pinho, 2011). Figure 2-1 shows a cross-section of a typical grinding machine used in mechanical recycling. Then, the collected pieces are roughly sorted using a separator, like cyclones or zigzag, into the powdery products (rich in matrix components) and the fibrous products (rich in recycled carbon fibres). Howarth et al. (2014) concluded that a higher recycling capacity of 150 kg/hr leads to lower energy consumption in 0.27 MJ/kg than does 2.03 MJ/kg at 10 kg/hr, and the unit milling energy accounts for a maximum of only 1.1 % of the embodied energy of virgin carbon fibre. Palmer et al. (2009; 2010) reported that the remanufactured SMC composite incorporated with milled CFRP recyclates shows a mechanical property comparable to the conventional SMC formulations if the volume fraction of the reinforcement is carefully controlled. However, the evident drawback of mechanical recycling is that the process cannot recover those valuable carbon fibres individually. Therefore, the recycled fibres are always contaminated with matrix residues and finite fibre length, which results in less competitive recyclate products and has already limited its reuse in the industry (Howarth et al., 2014; Liu and Tiwari, 2015; Yu et al., 2016).

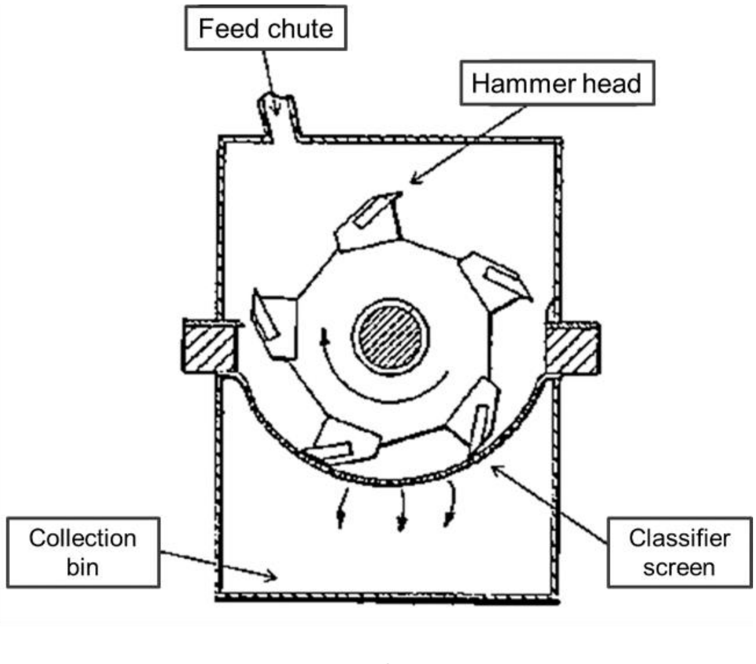


Figure 2-1 The cross-section of the mechanical hammer mill machine (Howarth et al., 2014).

2.3.2. Chemical recycling

In the chemical recycling process, chemical solvents, acid, alkali, and organic, are often involved in the separation of the fibre from waste composites by depolymerizing the resin matrix (Oliveux et al., 2015). This process can not only recover clean fibres, but it can also recycle the monomers from the depolymerized thermoset matrix, which are suitable as petrochemical feedstock (Liu and Tiwari, 2015). Chemical recycling is normally conducted at lab-scale and is expensive for industrial scale-up due to the demand for elevated pressure, high heat energy, and sometimes the use of hazardous chemicals. The suitable solvent strongly depends on the nature of the polymer (Jody et al., 2004). However, waste composite scrap still contains a complex mixture of various contaminants (Yang et al., 2012), which causes difficulties in chemical solvent selection. As chemical recycling can offer high-quality recycled fibres, many studies have been undertaken in this area. Early investigations focused on acid digestion, more recently supercritical fluids (SCFs) have been focused.

2.3.2.1. Acid digestion

Nitric acid is an inorganic and corrosive liquid, which is used especially as an oxidizing agent in nitration, and in making organic compounds such as fertilizers, explosives, and dyes. Due to its highly corrosive and strong acidic properties, it is feasible for use to degrade some organic material. The decomposition process through the nitric acids recycling method is shown in Figure 2-2. Recycling of pure epoxy resin using nitric acid was first proposed by Dang et al. (2002). The amine cured bisphenol F type epoxy resin was decomposed completely into high molecular weight intermediate solid and liquid in nitric acid solution at 80 °C (Dang et al., 2002). To investigate the degradation ability of various acids to epoxy resin, Liu et al. (2004) proved that nitric acid is stronger than sulfuric and hydrochloric acid, and then optimized conditions at 90 °C with 8 mol/L nitric acid solution along with a ratio of 4 gram carbon/epoxy composites to 100 ml of that solution. Similar research by Ma et al. (2009) reported that amine cured epoxy was decomposed to 99.18 % resin after 23 hrs at 95 °C in a 8 mol/L nitric acid solution (Ma et al., 2009). Lee et al. (2011) recycled the carbon fibre by using nitric acid in 8-14 mol/L and confirmed that the recovered fibres had retained 97% tensile strength of virgin fibres. The applicability of using nitric acid in sorting out glass fibre from waste thermoset GFRP was also investigated (Dang et al., 2005), it was found that glass fibre reinforced bisphenol F type epoxy resin (BPF) cured with diamino diphenylmethane (DDM) composite had successfully separated glass fibre from BPF/DDM epoxy resin at 70-90 °C. Hence, for BPF epoxy-based composite, a nitric acid solution also shows good performance for recycling fibre at a high temperature range.

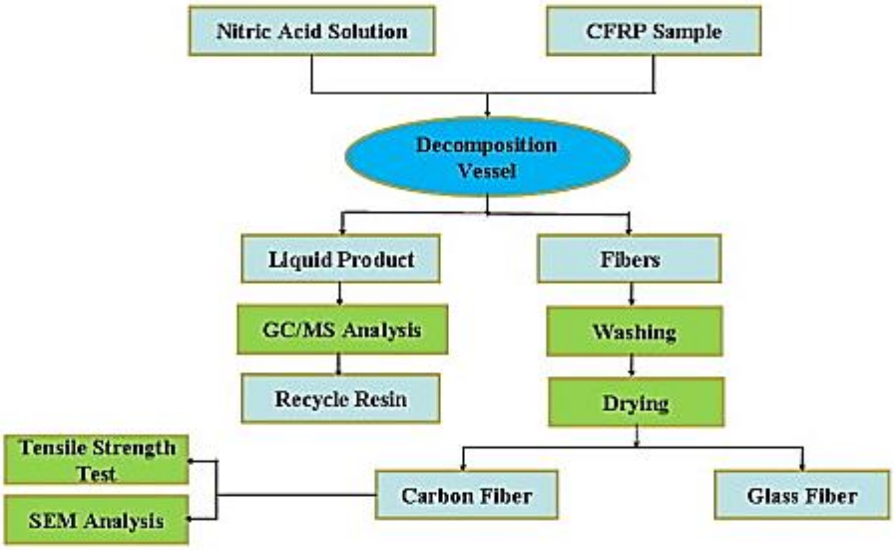


Figure 2-2 Chemical recycling process by acids (Liu et al., 2009).

2.3.2.2. Supercritical fluid (water and alcohols)

Chemical recycling using supercritical fluids (SCFs) is a developing technology which has been applied to waste thermoset composite. The supercritical fluids (SCFs) are the substances that when the temperature and pressure exceed their critical point, they have the ability to perform decomposition and partial oxidation in chemical reactions (Jiang et al., 2009). Water and alcohol are two widely used fluids in the recycling of CFRP or GFRP in sub-critical and supercritical conditions (Morin et al., 2012). Piñero-Hernanz et al. (2008a) studied the chemical recycling of

CFRP using water at supercritical or near-critical conditions in a batch-type reactor. The optimum supercritical condition was obtained at the pressure of 28 MPa and a temperature of 400 °C, which could increase the resin degradation ratio to 79.3 %. The recycled fibres showed a 90 % - 98 % tensile strength compared to that of the virgin fibres. Bai et al.(2010) successfully recovered the carbon fibres from CF/EP composites in supercritical water with oxygen at 30 ± 1 MPa and 440 ± 10 °C. The clean carbon fibres were recovered and showed similar tensile strength as that of virgin fibres when the resin decomposition rates were between 94 and 97 wt.%. Liu et al. (2009) achieved a completed degradation of epoxy resin in subcritical water and obtained the clean rCF with only 1.8 % reduction in tensile strength compared to that of virgin fibre. In subcritical water, carbon fibres were successfully recycled by a synergistic effect of the combination of phenol and potassium hydroxide (KOH) catalyst (Liu et al., 2012). This effect has been explained as the result of moderate phenoxy radicals from phenol benefiting the chemical bonds cracking in the crosslinked network of the cured epoxy resin (Liu et al., 2012). The dissolving capacity of methanol, ethanol, propanol, and acetone for CFRP has been investigated at the University of Nottingham (Piñero-Hernanz et al., 2008b). The process worked both in batch and in semi-continuous mode at temperatures ranging from 200 to 450 °C. Alkali catalysts, i.e., NaOH, KOH, and CsOH were introduced to improve the degradation process in a flow system with flow rates in the range of 1.1 to 2.5 kg-alcohol/kg-fibre/min. Alkali catalysts from 0.016 to 0.50 M were concentrated enough to degrade more than 95 % of the resin in less than 15 minutes. SEM analysis showed insignificant resin residues on fibre surfaces, and tensile strength tests demonstrated high strength retentions of 85–99%. Jiang et al. (2009) proved that there is no significant difference in the tensile strength of various fibres recovered from soaking CF/EP composite in a 310 °C supercritical n-propanol for 20 minutes. Okajima et al. (2014) separated the clean carbon fibre from CFRP using supercritical methanol at 270 °C and 8 MPa for 90 minutes. The tensile strength of rCF reduced by 9 % compared with that of virgin fibre. Supercritical fluid recycling technology will continue to draw attention from the research community for its recovery of not only clean carbon fibre with high mechanical property retention, but also polymer resin with high potential to be reused as a monomer for another chemical process. However, the main challenge is the high cost associated with achieving the high pressure and temperature requirements.

2.3.3. Fluidized bed process

The fluidized bed (FB) process recovers only the fibre, while the polymer matrix is incinerated for energy recovery. The University of Nottingham polymer research group has designed and developed a fluidized bed thermal process for recovering high-grade carbon fibre from carbon fibre reinforced composites scrap (Pickering, 2006). The fluidized bed technique is a process which suspends a number of solid particles in a flowing fluid with a specific velocity, making the particles have some characteristics similar to a flowing fluid. The advantages of the fluidized bed process are: High tolerance to contamination, nearly no residue on the fibre surface, high heat transfer rate, and high process reliability (Pimenta and Pinho, 2014). The fluidized bed (FB) process for carbon fibre recycling is particularly suitable for contaminated end-of-life components for its natural segregation property (Pimenta and Pinho, 2011). In the FB recycling process, small-sized composite scrap is fed into a bed of silica sand. The hot air with a temperature of around 450-550 °C fluidizes the sand and decomposes the polymer (Pickering, 2006; Yip et al., 2002). The released fibres are carried upward with the outgoing gas stream, while other heavier contaminants, such as metals, sink to the bottom of the bed. The recovered fibres are separated from the air stream in a cyclone, and the remaining volatiles are fully oxidized in a secondary combustion chamber (Pickering, 2006; Pimenta and Pinho, 2011). The process diagram is shown in Figure 2-3. The single fibre testing result shows that the mean length of recycled carbon fibre is 10 mm and their tensile strength retained around 75 % compared with the virgin fibre. In addition, Young's modulus remained unchanged and the surface of recycled carbon fibre shows only a small reduction in oxygen content and does not show any measurable oxidation of carbon fibre (Pickering, 2006; Yip et al., 2002).

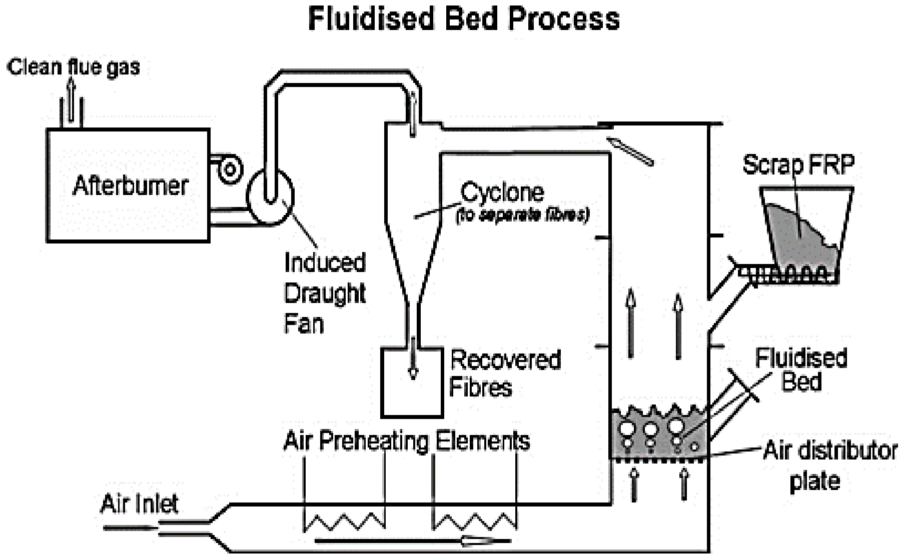


Figure 2-3 Fluidised bed recycling process (Wong et al., 2010).

2.3.4. Pyrolysis

Pyrolysis is a heating process conducted in absent of air. The polymer matrix is degraded into pyrolytic gas, oil, and char retained on the fibre surface. Pyrolysis can be classified as conventional or microwave on the basis of their different heating principles. Conventional pyrolysis usually treats the composite in an electric furnace and the material is heated by heat conduction and convection. Microwave pyrolysis is a special case whereby the material is heated using microwave energy. Microwave heating is a selective and rapid heating method. The polymer matrix is similarly degraded into gas and condensable volatile as the conventional pyrolysis, but theoretically takes a short processing time. Conventional and microwave pyrolysis are reviewed in detail in Sections 2.4 and 2.5 as the research is mainly focused on these two technologies.

2.3.5. Conclusions about existing processes

In this section, three recycling technologies for recovering clean fibre waste were concretely reviewed. They are identified as mechanical recycling, chemical recycling, and fluidised bed processing. Mechanical recycling is the earliest and the most energy efficient technology, but it is difficult to recover clean individual fibres separately. Carbon fibre recovered from mechanical recycling is severely polluted by the resin matrix shard and can only be used in some low-value applications, such as fillers. Chemical recycling methods have the strong capability to recover high-quality carbon fibre, but the demand for elevated pressure, high heat energy, and sometimes the use of hazardous chemicals, makes it an expensive process for industrial scale-up. The fluidised bed process has been developed over the past decades and is particularly suitable for EOL components and contaminated waste, however, carbon fibres recycled from this process exhibit relatively low mechanical properties. The processes classified as microwave pyrolysis and conventional pyrolysis were introduced and the details will be reviewed in Sections 2.4 and 2.5.

2.4. Conventional pyrolysis recycling process

Conventional pyrolysis is the most widespread process for recycling of CFRPs waste. The process is available on an industrial scale and involves a thermal decomposition process for organic polymer in the absence of oxygen (Emmerich and Kuppinger, 2014; Pimenta and Pinho, 2011). Figure 2-4 illustrates the main functioning steps of conventional pyrolysis. Waste CFRP scraps are fed into the reactor vessel and are heated up to the range of 500 – 800 °C in an inert gas atmosphere (e.g., Argon, N_2) (D. Akesson et al., 2012; Marsh, 2008). The polymer matrix is broken down into low molecular weight volatile matters and solid char product (D. Akesson et al., 2012; Marsh, 2008). Both carbon fibre and polymer matrix can be recovered in conventional pyrolysis, in which the polymer matrix is converted into three physical forms, i.e., solid char which remained on the carbon fibre surface, gas, and liquid recyclates. To obtain the clean recycled fibres, an extra oxidation or gasification stage is always applied to eliminate the char residue. The gaseous and liquid products are collected downstream and can potentially be reused as fuel or low molecular weight chemical feedstock.

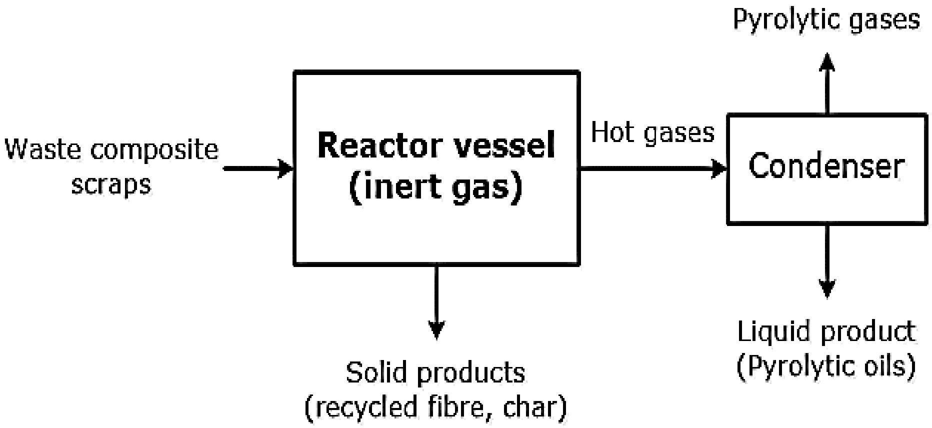


Figure 2-4 A typical conventional pyrolysis process.

2.4.1. Recycled carbon fibre properties

It is common to have an extra oxidation stage to eliminate the pyrolytic char in conventional pyrolysis, while the carbon fibres undergo the same oxidation condition. Therefore, the mechanical and surface properties of recycled fibre are the effective parameters to evaluate if the carbon fibre is damaged during the recycling process. The two stages, consisting of the degradation of polymer resin and the oxidation of pyrolytic char, represent a standard conventional recycling process. The composite waste fragments were firstly pyrolyzed at 600 °C for 60 minutes in a nitrogen atmosphere (Song et al., 2017) and then air was introduced at the same temperature for 60 minutes. The rCFs showed a smaller diameter and reduced tensile properties as the oxidation time extended, but a cleaner surface. The increased oxygen-containing functional groups of the rCFs indicated that reaction happened between the carbon fibre and oxygen. López et al. (2013) recovered carbon fibre via a combined process of thermolysis and gasification in an air at 500 °C. The rCFs retained 70 % of tensile strength and 90 – 96 % of elasticity of that of the virgin fibres. They stated that the longer gasification time led to an undesirable change on fibre surface atomic composition. Mazzocchetti et al. (2018) oxidized the char residue on fibre at 500 °C – 600 °C for 10 – 60 minutes to obtain the clean fibres after a pyro-gasification process in a pilot plant. The diameter of the rCFs reduced with the increase of either oxidation temperature or time, however, the mechanical properties of composites reinforced by chopped rCFs were competitive with that of virgin fibre composites. Jiang et al. (2016) investigated the surface property of rCFs recovered from prepregs using pyrolysis at 500 °C and then oxidation in air. They stated that oxidative and thermal effects are significant factors affecting the properties of rCFs. The oxidative effect results in surface defects and cause a further reduction in tensile strength. The thermal effect results in a decrease in surface oxygen content leading to a poor surface bonding with the polymer matrix. Onwudili et al. (2013) concluded that the mechanical properties of the recovered fibres were lower than those of the virgin fibre for carbon fibre recovered from CFRP using pyrolysis. A similar result for glass fibre has been reported by Cunliffe et al. (2003a). Ma et al. (2020) studied the influences of operating temperature, oxygen concentration, and superheated steam on the mechanical and surface properties of rCFs. The results showed that the presence of oxygen or superheated steam and higher temperatures have negative effects on the tensile strength of recycled carbon fibre. The rCF preserved 94% of the original tensile strength at 500 °C due to the protective effect of pyrolytic char. And the tensile strength of rCF declined rapidly when the temperature was raised to 550 °C and 600 °C.

Some industrial-scale conventional pyrolysis for CFRP waste has been reported. ELG Carbon Fibre developed a thermal pyrolysis process to treat contaminated carbon scrap waste (Marsh, 2008). Thermoset scraps comprise epoxy, bismaleimide, phenolic, and others; these were cut into 200 mm × 250 mm × 25 mm pieces. Then the materials were heated in a reduced oxygen atmosphere at high temperature to degrade the polymer matrix. The rCFs were free of sizing and retained 80 % – 90 % of the mechanical properties of the virgin fibre. Furthermore, ELG and other research institutes recycled glass and carbon fibres and reused them as the reinforcement for LDPE matrix (Onwudili et al., 2016). In Germany, CFRP scraps were cut into 12 cm x 6 cm x 4 mm pieces and were pyrolyzed in an oven at 600 °C for 80 minutes (Emmerich and Kuppinger, 2014). The rCFs had reductions of 11.3 % in diameter and 35.7 % in tensile strength. However, the tensile modulus increased 17 %.

2.4.2. Pyrolytic char properties

During pyrolysis of carbon fibre composite, polymer degradation produces pyrolytic oil, gas, and pyrolytic char, which are retained at the fibre surface. The rCFs are contaminated by pyrolytic char which prevents a good adhesive with the matrix in reuse applications. A post-treatment of char elimination is always required to obtain the clean carbon fibre, but this leads to some damage of the fibres. Thus, better understanding of pyrolytic char formation is imperative, not only for reducing char yield, but also for preserving better mechanical performance of rCFs. Some research has reported that the yield of solid products (char and fibre) varied with the pyrolysis parameters. Torres et al. (2000) reported that the solid residues of pyrolysis of polyester based sheet moulding compound (SMC) at 300 – 700 °C for 30 min was 72 – 82 wt.%, in which 25 wt.% was glass fibre. Onwudili et al. (2013) analysed the pyrolytic char yield from pyrolysis of polybenzoxazine-based CFRP between temperatures of 350 – 500 °C. The pyrolytic solid residue yield was 72 – 77 wt.%, in which the solid residue has 98 wt.% carbon fibre. Pei et al. (2013) proved that the amount of pyrolytic residue generated by pyrolysis of plastic waste (PE, PP, PVC) reduced as the heating rate increased. Another study reported on the analysis of the properties of char derived from HDPE plastic pyrolyzed at temperature of 400 – 450 °C (Jamradloedluk and Lertsatitthanakorn, 2014). Elemental analysis showed that pyrolysis char had a large proportion of carbon and some small amounts of inorganic elements. The BET surface area and specific pore volume were analysed and reported to 10.83 m^2/g, 0.1441 cm^3/g, respectively. Their research confirmed that pyrolytic char can be activated and used as fuel (char-based briquette) as the calorific value of the char was 4 500 cal/g.

2.4.3. Pyrolytic gas and oil properties

In the pyrolysis process, a large proportion of the polymer matrix is converted into pyrolytic oil and gas product collected downstream which contains some valuable chemical feedstock and combustible gas. Concerning the fuel and energy recovery, some researchers pay more attention to the characterization of pyrolytic oil and gas product derived from the polymer matrix. Torres et al. (2000). investigated the pyrolytic product of pyrolysis of glass fibre reinforced polyester composite at 300 – 700 °C for 30 minutes, and found that there was no significant effect on the product yield and composition when the temperature was over 400 °C. The main components of pyrolytic oil were aromatic and oxygenated compounds, which have high gross calorific values of around 34–37 MJ kg^{-1}. The gas products were rich in CO and CO_2, which had a relatively low calorific value. Onwudili et al. (2013) pyrolyzed the polybenzoxazine resin based carbon fibre composite in an autoclave at temperatures in the range of 350 –500 °C, and reaction times of up to 60 minutes. The pyrolytic products had the solid residue yield of 72 – 77 wt.%, gas yield of 2 – 4 wt.%, and liquid yield of 22 – 25 wt.%, in which the solid residue had 98 wt.% carbon fibre. The gas products contained mainly CO_2 and some hydrocarbons, which had a maximum calorific value of 35 MJ/m^3.

The liquid products consisted of water (15–20 wt.%) and oil. The major components of the oils included aniline, methyl aniline, and phenols. A glass fibre reinforced thermoset polyester composite was pyrolyzed in a fixed-bed reactor at 450 °C by Cunliffe and Williams (2003a). The main gas products were CO, CO_2, H_2, CH_4, and other hydrocarbons from C_2 to C_4, in which CO and CO_2 occupied over 75 vol% of the total gas. The oil products included styrene and phthalic anhydride, which could potentially be recycled into polyester resins.

2.4.4. Pyrolysis parameters

The fibre properties and product yield from pyrolysis of composites are affected by the different pyrolysis conditions. Various parameters comprising polymer matrix, pyrolysis temperature, time, and gas atmosphere are important parameters, which affect the pyrolysis process and were investigated in some research.

2.4.4.1. Types of polymer matrix

The pyrolysis temperature and time depend strongly on the degradation properites of a polymer matrix. For example, this is seen in the different heat resistance of thermoset and thermoplastic resin. Cunliffe et al. (2003a) investigated pyrolysis of composite plastics in a fixed bed reactor at temperatures between 350 – 800 °C. The polyester

(PES), phenolic (PF), epoxy (EP), polypropylene (PP), and Polyethylene terephthalate (PET) resins matrix reinforced with glass and/or carbon fibre composites were studied. The results showed that there was no obvious correlation between products of these compositions and the final pyrolysis temperature of polyester, phenolic, and epoxy composites. The tensile strength of recovered glass fibre was lower than that of virgin fibre and the reduction in strength was further aggravated with increasing pyrolysis temperature from 650 to 800 °C. Similar research (Cunliffe et al., 2003b) was performed by pyrolyzing the waste composites of glass and/or carbon fibre reinforced polyesters, phenolic, and epoxy resins at 350 – 800 °C. The results showed that the polymer matrix and pyrolysis temperature markedly influenced both the product mass balance and pyrolysis gas composition. The average molecular mass and mass of the pyrolytic oils were dependent on the polymer matrix.

2.4.4.2. Gas atmosphere

The controlled gas atmosphere was added to extract the fibre and minimize the char generated during the pyrolysis in the development of conventional pyrolysis. Yang et al. (2015) adjusted the ratio of oxygen in an inert nitrogen atmosphere and investigated the tensile strength of rCFs at different pyrolysis conditions. The results showed that char residue was preferably removed, and fibre had the optimum tensile properties at 650 °C in gas mixture of 5% O_2/ 95% N_2. They also demonstrated that the tensile strength of fibre could be affected by the oxygen concentration. Limburg et al. (2019) used a CO_2 and water vapour atmosphere during pyrolysis of CFRP. Their results showed that this atmosphere is capable of removing the char without visible fibre damage when temperatures increased to 1000 °C, which is the same point at which surface defects occurred on the fibre in a sole CO_2 atmosphere. This research provides a new possible method of char elimination in the carbon fibre recycling industries. Jeong et al. (2019) decomposed the resin in waste CFRP at 600 – 800 °C for 60 minutes using steam. The fibres were successfully recovered from waste CFRP and the rCF retained 65 % and 100 % of tensile strength and tensile modulus of vCF, respectively. A conventional pyrolysis in a vacuum environment with a catalyst has been developed by Adherent Technologies Inc. (Gosau et al., 2006). Scrap contaminated composites are treated by thermal vacuum pyrolysis, in which the plastic and all volatile components can be removed. Another wet chemical treatment is used to degrade the metal, and other inorganics which saves processing chemicals and clean-up cost. Any untreated matrix material can be removed in a high temperature wet chemical treatment, and all contaminate expect fibre can be decomposed.

2.4.5. Conclusions on pyrolysis methods

Conventional pyrolysis is the most common technology implemented in this research area and in commercial-scale applications. Conventional pyrolysis is capable of recovering both, carbon fibre and resin matrix, but there is a severe char deposition problem on the fibre surface. Though the char can be removed by extra oxidation, there is great potential for damage to the carbon fibres. The types of polymer matrix, temperature, heating rate, and gas flow rate are important factors which affect the quality of products in conventional pyrolysis. As the quality of rCF is sensitive to the pyrolysis conditions, the optimization of parameters need to be further investigated to reduce char formation as well as recover high-quality fibre. In consideration of the advantages in terms of energy saving and re-application, the analysis of gas and oil produced is necessary.

2.5. Emerging recycling technologies

In recent years, emerging recycling technologies have been proposed to make recycling more environmentally friendly and economically viable. For example, the usage of microwave pyrolysis could potentially shorten reaction time. The utilisation of Lewis acids could possibly help to recover the fibres at mild conditions. The following sections review the literature on these emerging recycling technologies.

2.5.1. Microwave pyrolysis

Conventional pyrolysis is the most widely used technology in the industry, however, it has its drawbacks. Conventional pyrolysis is carried out by heat conduction, convection, and radiation (Chen et al., 2008a), which suffers from heat transfer resistance and heat losses to the surrounding environment (Bridgwater, 1999). Another drawback is the low heating rate in electric/gas furnaces, which results in long heating duration and causes undesired or secondary reactions (Tian et al., 2011). Microwave technology has gained increasing interest due to its special heating nature that allows simple and rapid processing of materials (Clark and Sutton, 2003). In addition, microwave heating is a potentially more attractive technique because of its volumetric heating feature which improves heating efficiencies compared to conventional techniques (Appleton et al., 2005). In the microwave heating process, energy transfer occurs through the interaction of molecules or atoms. Therefore, microwave heating is also referred to as dielectric heating (Jones et al., 2002) which transforms electromagnetic energy to thermal energy, rather than heat transfer via conventional heating mechanisms (Thostenson and Chou, 1999). Table 2-1 lists the differences between conventional and microwave heating in pyrolysis. Compared with conventional heating, more uniform temperature is achieved, and undesired secondary reactions can potentially be avoided when using microwave heating (Santaniello et al., 2012).

Table 2-1 The comparison of conventional heating and microwave heating in pyrolysis.

	Conventional heating (Undri et al., 2011)	Microwave heating (Undri et al., 2011)
Reaction time	Longer (hours)	Shorter (minutes)
Heat transfer	Slow (Low thermal conductivity of polymer)	Fast (Low thermal conductivity of polymers may be negligible)
Heat efficiency	Hardly to obtained	High
Energy source	Electrical power/Fuel	Electrical power

Usually, the microwave reactor has two operating modes, the power control mode and the temperature control mode. In the former, the power output is held at a constant pre-set point for the entire set time of the process. The temperature of the materials is monitored to prevent overheating. The power control mode can potentially shorten heat-up time by allowing materials to reach a high temperature at a faster rate. In the temperature control mode, materials are heated from room temperature to a preselected temperature at a certain heating rate. The temperature is then held constant for certain periods of time. During the temperature increase and the dwelling period, the power output of the microwave radiation is regulated automatically by a feedback control loop via a PID controller. These operating modes are commonly used in the microwave heating industry.

Recently, microwave pyrolysis of composites has gained increasing interest from both academia and industry (D.Akesson and M.Skrifvars, 2011; Dan Akesson, 2013; McConnell, 2010; Ulven et al., 2014). The advantages of using microwave pyrolysis to recover carbon fibre are that it is energy saving (Lester et al., 2004), selectively heating (Peng et al., 2017) and highly efficient (Jiang et al., 2015) due to its higher heating rate and shorter heating time (Wu et al., 2014). As carbon fibre has a high dielectric constant which is sensitive to microwave heating, the carbon fibre in waste composite is heated directly by microwave energy and undergoes volumetric heating so that the heat transfer rate is relatively high potentially saving processing time and enabling energy savings (Emmerich and Kuppinger, 2014; Leeke et al., 2016). In microwave pyrolysis, CFRP waste is heated in an inert gas atmosphere and the resin matrix is cracked into gas and oil, whilst carbon fibre and char residue are recovered as the solid product at the end of the recycling process (Oliveux et al., 2015). By performing two different control parameters, i.e., controlled power or controlled temperature, researchers have carried out the carbon fibre recycling process using microwave heating. The chemical and physical properties of the recycled fibre, and its heating mechanism have been studied (Eltron Research & Development, 2009).

2.5.1.1. Controlled power

The feasibility of recycling using microwave pyrolysis was firstly reported by Lester et al. (2004). They successfully recovered carbon fibre from CFRP under microwave irradiation at 3 kW for 8 seconds: 98 wt.% of epoxy resin from a CFRP composite was removed, and the tensile strength of rCF decreased by around 20%. They stated that this method may offer a route to the recycling of longer fibre compared with the FB process. Obunai et al. (2015) investigated the resin elimination ratio in air, nitrogen, and argon in the pyrolysis of epoxy-based carbon fibre composite at constant power of 700 W. The resin elimination ratio in three gas atmospheres increased rapidly and steadied to around 90 % in the irradiation time of 1-200 seconds. However, the elimination ratio of resin was over 100 % in air as the time was further extended to 300 seconds, due to the fibre oxidation and damage. The rCF recovered in nitrogen or argon showed a smooth surface with little char residue, while damage was shown on that of rCF obtained in air. Obunai et al. (2015) suggested that argon is the most effective atmosphere to recover the fibre in balancing the resin elimination ratio and the fibre damage. In Germany, Emmerich et al. (2014) aimed to develop a carbon fibre recycling system using continuous power from microwave irradiation. They treated the CF prepreg at 600 W for 150 seconds and found that the sample thickness and microwave penetration depth is a considerable problem in industrial scale operations. The damage to rCF became more and more severe from the core to the outer layer of the prepreg.

2.5.1.2. Controlled temperature

Temperature is one of the crucial parameters in the pyrolysis process. Recycling of carbon fibre at a controlled temperature is a more effective and instructive way to prevent overheating and damage to the rCF. Jiang et al. (2015) found that 500 °C is the optimum temperature for microwave pyrolysis as an acceptable compromise between resin removal and fibre damage. The mechanical properties of rCF were not analysed, but the diameter reduced by 10-16 % compared to virgin fibre. Furthermore, as the new reinforcement, the rCF showed a better performance in nonpolar PP, while the virgin fibre dominated in polar Nylon; this could be ascribed to the fibre surface roughness and its surface bonding characteristics. Most recently, Deng et al. (2019) recovered the carbon fibre using microwave irradiation in a pure oxygen atmosphere and optimum temperature of 450 °C. The recovered fibre heated via microwave had a lower graphitization degree compared to that of fibre obtained via traditional heating. Besides, GFRP had also been pyrolyzed by microwave at the optimal temperature of 440 °C, while Akesson et al. (2012) reported that the tensile modulus of fibre decreased by about 28 %, and the composite made from recycled glass fibre and polyester resin showed a relatively low mechanical performance.

2.5.1.3. Mechanism of microwave heating of carbon fibre composite

Many researchers have proven that microwave pyrolysis is an effective way to separate the fibre from polymeric composites, but the clear mechanism of the decomposition of composite under microwave irradiation is only investigated by Obunai et al. (2015). They used model specimens in which carbon fibre was embedded in epoxy resin to verify the mechanism of microwave heating of carbon fibre composite. They proposed that the process can be divided into three stages. First, the carbon fibres in CFRP were Joule heated by induced current by microwave irradiation. Then, the gasification of resin was promoted by the heated carbon fibres. Finally, the gasified resin was decomposed by spark glow plasma induced by spark glow discharge between carbon fibres.

2.5.2. Lewis acid at mild conditions

Unlike in the past, the milder environment have been reported recently instead of the usage of strong acid (Dang et al., 2005) or alkali solution (Liu et al., 2012) in dissolving epoxy matrix in chemical recycling approach. The degradation solutions consist of the Lewis acids, such as zinc chloride ($ZnCl_2$), magnesium chloride ($MgCl_2$), aluminium chloride ($AlCl_3$), and solvents like water, ethanol, acetone, and acetic acid. Liu et al. (2017) reported that a CFRP waste (Tg > 210 °C) is effectively decomposed in a $ZnCl_2$/ethanol (20 wt.%) catalytic system at 190 °C for 5 hours. The resin degradation is 89.8 %. Deng et al. (2015) studied the degradation effect of chlorides aqueous on cured epoxy at mild temperatures (170 – 220 °C). At 220 °C for 9 hours, they found that, compared with $MgCl_2$, $FeCl_3$, and $CuCl_2$ aqueous, 60 wt.% $ZnCl_2$ aqueous indicated a stronger degradation ability on the cured epoxy at

97.3 % degradation. Keith et al. (2018) demonstrated that the $ZnCl_2$/acetone/water system was a valid catalyst to dissolve more than 94% epoxy resin and that the process period could be shortened with higher temperatures from 90 to 45 minutes by increasing the temperature from 290 °C to 300 °C. Furthermore, the epoxy composites could be completely dissolved in molten $ZnCl_2$ at 360 °C in 80 minutes under standard pressure, which was a result of the fracture of the C–N bonds in the epoxy matrix by the catalytic action of Zn^{2+} ions (Wu et al., 2019).

In conclusion, these studies all mentioned that the catalytic degradation ability of $ZnCl_2$ comes from the incompletely coordinated Zn^{2+} ions, which could selectively cleave the C-N bond without breaking C–C and C–O bonds in epoxy. Based on the superior reusability of concentrated $ZnCl_2$, it is also suggested that this method could effectively recover the carbon fibre and the valuable unit of EP from CF/EP composite waste. Additionally, another catalytic recycling system using $AlCl_3$ and CH_3COOH was developed and over 97.4 wt.% epoxy was recovered from 15 wt.% $AlCl_3$/CH_3COOH solution at 180 °C for 6 hours. Meanwhile, the recycled carbon fibre still retained 97.77% of its tensile strength compared with virgin fibres (Wang et al., 2015a). To obtain cleaner fibre, a two-step method to recover fibres from CF/EP composite under mild conditions was reported by Xu et al. (2013). In their research, acetic acid was first used to expand the resin matrix. Secondly, the treated composite was immersed in a mixed solution of hydrogen peroxide (H_2O_2) and dimethylformamide (DMF) at 90 °C for 30 minutes in a hermetic reactor. This process achieved the degradation rate of over 90 % of resin in waste composite and retained 95 % tensile strength of rCFs compared to virgin carbon fibre.

Besides epoxy, chemical decomposition of unsaturated polyester resin (UPR) and its GFRP were effectively decomposed and recycled by using the $AlCl_3/CH_3COOH$ system (Wang et al., 2015b). The degradation result showed over 91 wt.% of monomers and oligomers were recycled from UPR, and the glass fibre was successfully recycled in 10 wt.% $AlCl_3/CH_3COOH$ solution at 180 °C in 9 hours. They concluded that the high efficiency of the $AlCl_3/CH_3COOH$ system for decomposing UPR from not only the catalytic effect of $AlCl_3$, but also the participation of acetic acid in the reaction. The $AlCl_3/CH_3COOH$ system was able to selectively cleave the C–O bond in ester chains of UPR and retain the intact carbon skeleton at the same time. During the degradation process, $AlCl_3$ also interreacted with the C=O bond, which could promote the reaction between acetic acid and the ester bond of UPR.

Usually, thermoplastic polymers are recycled by remoulding or reshaping, but the chemical degradation method was also proposed recently. Wang et al. (2019b) investigated the degradation of polyethene terephthalate (PET) using $ZnCl_2/H_2O$ solution. In their research, PET was degraded in 70 % $ZnCl_2/H_2O$ catalyst solution with a degradation ratio of up to 100%. High-value-added terephthalic acid (TPA), with a purity of around 97%, was reclaimed from PET at 180 °C for 8 hours. The study also confirmed that the effective decomposition by the catalyst system should be attributed to the coordination and catalysis of Zn^{2+} ion.

2.5.3. Conclusions on emerging methods

Two emerging recycling technologies have been reviewed, i.e., microwave pyrolysis and chemical degradation using Lewis acid. Microwave pyrolysis has gained more recent interest for the instant, selective, and volumetric nature of microwave heating, and is increasingly being applied to recycle carbon fibre. The first report on the feasibility of using microwave pyrolysis to recycle carbon fibre was showed by Lester et al. (2004). Since then, there has been little literature about this technology until now. It has been shown that carbon fibres can be successfully recovered under microwave irradiation at either controlled power or controlled temperature levels. The recycled fibre shows competitive mechanical properties to fibre recovered from conventional pyrolysis, and the processing time is greatly shorter than that of chemical recycling methods. Lewis acid provides a milder solution for degrading the polymer matrix in composites via the selective cleavage of the chemical bond. The Lewis acid catalytic systems are proved to be able to selectively cleave the C-O bond in UPR (Wang et al., 2015b) or the C-N bond in epoxy (Liu et al., 2017), in the temperature range of 170 – 220 °C. While this method providing a milder environment which potentially preserves the mechanical properties of carbon fibre, a long processing time is always applied. The particular Lewis acid needs to be selected for the target chemical bond as well as the specific polymer resin, therefore this method is not proper for treating the contaminated waste at present. In summary, these emerging methods still need to be systematically investigated in the future.

2.6. Overall conclusions and prospects

Various recycling technologies for recovering clean fibres from CFRP waste have been theoretically reviewed. A mechanical recycling process is the earliest and most energy-saving technology, but the severely polluted recycled fibres can only be used in some low-value applications. Chemical recycling methods have strong capability to recover high-quality carbon fibre, but the demands of elevated pressure, high heat energy, and sometimes the use of hazardous chemicals, makes its process expensive for industrial scale-up. The fluidised bed process has been developed over recent decades and is particularly suitable for EOL components and contaminated waste. However, carbon fibres recycled from this process exhibit relatively poor mechanical properties.

Conventional pyrolysis is the most wide-spread technology for recycling polymer composites in both academia and industry. Conventional pyrolysis is able to recover both carbon fibre and resin matrix, but the extra oxidation for char elimination potentially damages the recycled fibres. Thus, the char reduction during the pyrolysis process, and char elimination without compromise to mechanical performance of the recovered carbon fibre, are inherit problems in conventional pyrolysis.

Microwave pyrolysis is gradually being applied to recycle carbon fibre and is potentially able to shorten the processing time and save energy. The carbon fibres can be successfully recovered at either controlled power or controlled temperature and show competitive mechanical performance to that of fibre from conventional pyrolysis. Furthermore, the processing time is much shorter than that of the chemical recycling method. Lewis acid provides a solution for recycling carbon fibre via the selective cleavage of the chemical bond in resin. Despite this method providing a milder environment and potentially preserving the mechanical properties of carbon fibre, a long processing time is always applied. The particular Lewis acid needs to be selected for the targeted chemical bond in a specific polymer resin, therefore this method is not suitable for treating contaminated or mixed waste at present.

In summary, despite the fact that conventional pyrolysis is well-established in industry, pyrolysis parameters for recycling carbon fibres have not been well optimized to recover the best products with the least energy consumption. Certainly, the pyrolysis process has an inherited challenge in managing char elimination without compromising the mechanical performance of the recovered fibres. Meanwhile, the extra char elimination process increases the energy cost. Therefore, the optimization of conventional pyrolysis parameters and the development of a new recycling method, which are capable of reducing char formation significantly during pyrolysis reactions, needs to be studied further and more deeply. In addition, microwave pyrolysis is proved to be an effective method for recovery of the carbon fibre and potentially saves energy. Previous research is limited, most has been implemented under a single pyrolysis condition and demonstrates a lack of analysis of pyrolysis variables and product properties in the microwave pyrolysis recycling process. Therefore, a systematic analysis of the influence of different microwave pyrolysis conditions on product distribution and properties is important for future research.

Chapter 3. Materials and Experiments

3.1. Introduction

In this research, the optimization of conventional pyrolysis was first investigated using thermal analysis of prepregs. Various pyrolysis conditions and char analysis were applied to reduce the char formation and understand char oxidation behaviour. Then, a new hybrid method, one which starts with a chemical pre-treatment process and follows with a conventional pyrolysis, was proposed to reduce or remove the char formation, particularly in conventional pyrolysis. Then, the microwave pyrolysis was carried out as a possible new replacement for the conventional pyrolysis process to recycle carbon fibre. It has the advantage of a fast heating rate and potential energy saving from microwave heating. The research route is shown in Figure 3-1. The detailed materials, methods, and characterizations for the research are introduced in this section.

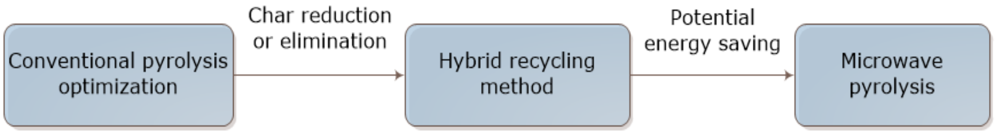


Figure 3-1 The main route of this research.

3.2. Optimization of conventional pyrolysis

Conventional pyrolysis is a widely used technology to recycle the carbon fibre, but the severe char deposition on the fibre surface is an inherent problem. To reduce the pyrolytic char formation and understand its oxidation behaviour, various pyrolytic conditions in terms of heating rates, temperatures and nitrogen gas flow rates were applied to two types of thermoset prepregs. The char residues derived from the two different thermoset resins were subjected to the intrinsic reactivity analysis during TGA, elemental composition determination using EDS, surface area and pore size measurement by BET surface analysis and morphology study using SEM. After the investigation, the optimum pyrolysis condition for the lowest char content was applied to chemically pre-treated thermal pyrolysis described in Section 3.3. The detailed materials and method are introduced in followed sections.

3.2.1. Materials

Two unidirectional prepreg i.e. carbon fibre reinforced epoxy (CF/EP) prepreg and carbon fibre reinforced phenolic (CF/PF) prepreg were used in this experiment. The unidirectional CF/EP prepreg composing of Toray$^{@}$ T700s carbon fibre and Bisphenol-A epoxy resins was supplied by Aojing$^{@}$ Composite Company, Shanghai, China, and contained 37 wt.% of epoxy resin according to the datasheet. The unidirectional CF/PF prepreg consist of Toray@ T700s carbon fibres and Resol-phenolic resin was supplied by Hengshen Fibre Materials company, Jiangsu, China, and contained 34 wt.% of phenolic resin according to manufacturing data. The CF/EP and CF/PF prepregs were first cut to a size of 200 mm×200 mm and then cured at 140 °C for 2 hours and 130 °C for 3 hours respectively in an atmospheric oven according to manufacturers' specification. After curing, the prepregs were collected and stored in a dry environment. Release film and backing paper were removed before the prepregs were subjected to thermal analysis using a thermogravimetric analyser.

The corresponding neat epoxy and phenolic resin of two prepregs mentioned above were used to study the pyrolytic char formation and its oxidation behaviour. To obtain solely the two types of resin i.e. epoxy and phenolic, the as-received epoxy and phenolic prepregs were compressed under a pressure of 5 MPa using a ZG-50 T press at 80 °C respectively. The squeezed-out resin was collected and cured at the same curing conditions as the above prepregs.

3.2.2. Experimental method

To optimize conventional pyrolysis and understand the pyrolytic char formation and its oxidation behaviours of thermoset composite, two types of cured prepregs, i.e. CF/EP prepreg and CF/PF prepreg were pyrolyzed in an SDT Q600 thermogravimetric analyser (TGA, Figure 3-2) supplied by TA instrument, USA. The thermal treatment profile is depicted in Figure 3-3. It began with a heating stage using four different linear heating rates, i.e. 20, 80, 100 and 200 °C/min, to heat the sample from room temperature to either 550 °C or 650 °C. Then the temperature was maintained for 30 minutes. These all happened under a nitrogen-filled atmosphere, with a flow rate of 50 ml/min. Finally, the tests were completed with a natural cooling stage. In the later stage of the study, the effect of nitrogen gas flowrate rate on pyrolytic char content was investigated by increasing the flow rate from 50 ml/min to 100, 200 and 400 ml/min, using the same range of heating rate and pyrolysis temperature. Measurements were carried out on approximately 20 mg of samples and their weight loss profile was recorded and analysed. The same isothermal condition was maintained for the next 60 minutes, but the nitrogen gas was replaced with a hot air purging, also at 50 ml/min, for an oxidation study on the formed pyrolytic char. Each test in TGA has been repeated three times, and the average value was calculated and analysed.

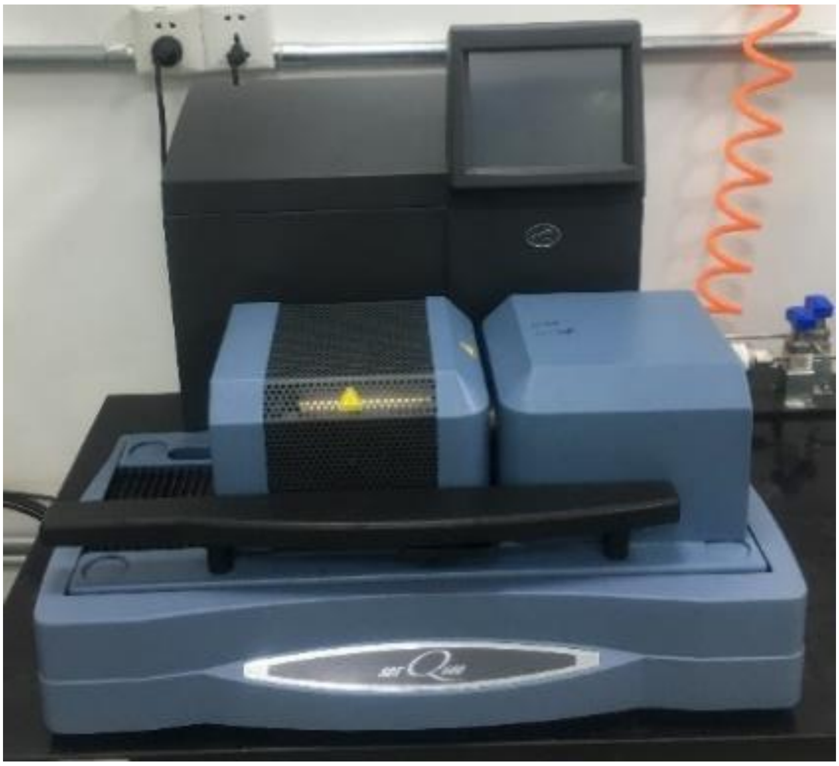


Figure 3-2 Thermogravimetric analyser (TGA).

The neat and cured epoxy and phenolic resins were subjected to the same pyrolysis process as the prepregs, as shown in Figure 3-3, for the generation of pyrolytic chars, however, the nitrogen gas flow rate was maintained at 50 ml/min as it was identified this study later that char content was not dependent on the flow rate. The pyrolytic chars were later dried and subjected to intrinsic reactivity test and other characterizations, as detailed in Section 3.2.4.

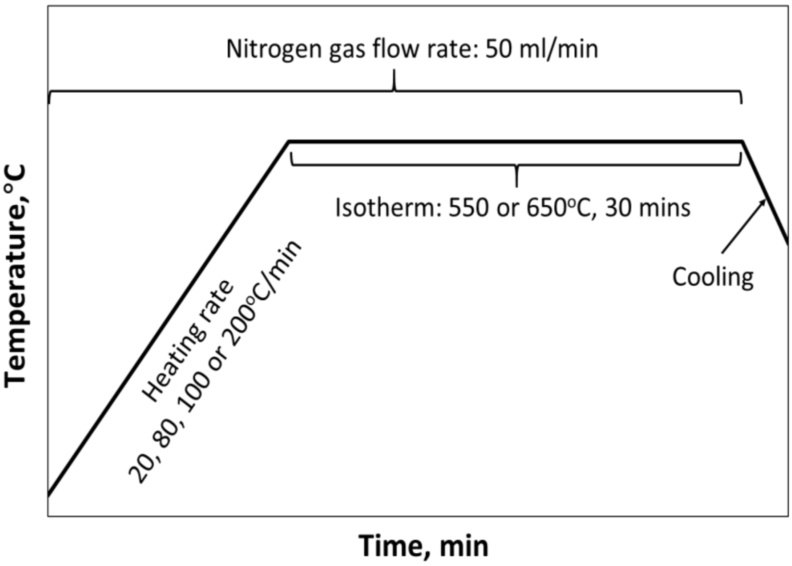


Figure 3-3 Thermal treatment profile used in the TGA test.

3.2.3. Analysis of pyrolytic char content

The effects of pyrolysis conditions on thermal degradation of prepreg, particularly the amount of char generated from the epoxy resin and phenolic resin were investigated in a TGA. The different heating rate, temperature, and gas flowrate of pyrolysis conditions were analysed. The TG curve of pyrolysis of CF/EP prepreg and CF/PF prepreg should be expected as examples shown in Figure 3-4. Since pyrolysis treatment hardly affects the carbon fibre, the weight of residue consists of the weight of carbon fibre provided by the prepreg vendor and char content. The char content(wt.%) is calculated by subtracting the weight of carbon fibre form residue, as showed below:

$$W_C = W_R - W_{CF}$$

Where W_C is the char content (wt.%),

W_R is the weight of residue(wt.%),

W_{CF} is the weight of carbon fibre(wt.%).

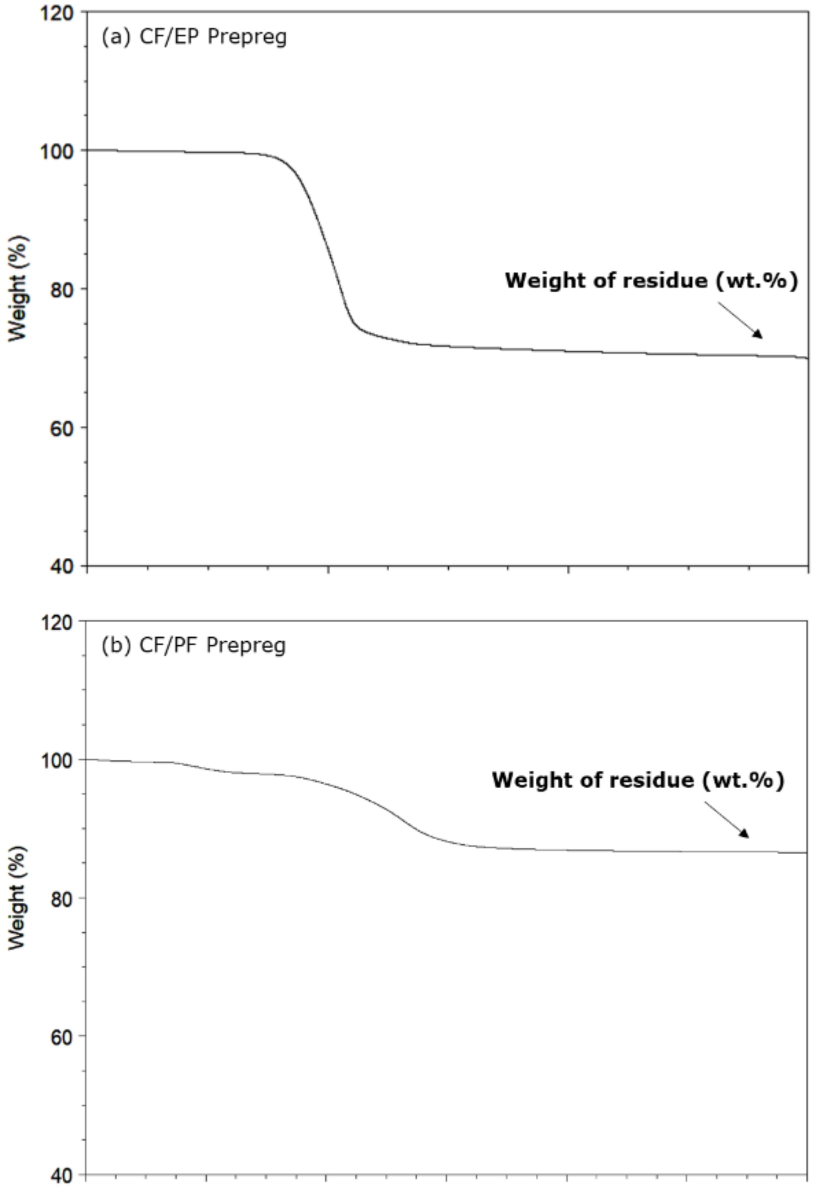


Figure 3-4 Expected TG curve of pyrolysis of (a)CF/EP and (b)CF/PF prepreg.

3.2.4. Characterization of pyrolytic chars

In the oxidation behaviour analysis, carbon fibre and char are primarily carbonaceous residue materials, both are oxidised at the same time at high temperature, making it difficult to solely focus on char oxidation behaviour investigation. Therefore, in this study, the extracted neat resins described in Section 3.2.1 were pyrolyzed using the same range of pyrolysis treatments as the prepregs, to create chars, which were free of carbon fibre. The pyrolytic char generated from epoxy resin and phenolic resin were characterized using the methods described in the below sections.

3.2.4.1. Intrinsic reactivity analysis

It is commonly accepted that the combustion characteristic of carbonaceous residue can be determined by using an intrinsic reactivity analysis with a non-isothermal heating method in the air (Unsworth, 1991). A heating rate of 20 °C/min was used to heat the pyrolytic char sample from room temperature to 105 °C and was held for 30 minutes for moisture removal in the presence of air. The temperature was then raised to 900 °C with the same heating rate and in an air-filled environment to complete the intrinsic reactivity study. Mass loss profile (TG) and the first derivative of the mass loss profile (DTG) were analysed to identity peak temperature (PT) and burnout temperature (BT) of the pyrolytic char sample. Peak temperature can be determined from the peak of the DTG curve, which is the temperature at which the rate of combustion is the greatest. The temperature at which the rate of decomposition drops to 1 wt.%/minute is known as the burnout temperature.

3.2.4.2. BET surface area and pore size

The Brunauer–Emmett–Teller (BET) specific surface area and pore size of pyrolytic chars generated at different heating rates and pyrolysis temperatures were determined by nitrogen adsorption at 77.35 K by using an ASAP 2020M automatic adsorption analyser supplied by Micromeritics Instruments, US. The relative pressure was 0 to 1. The specific surface area and pore size of the test samples were recorded.

3.2.4.3. Surface electron morphology

Surface morphology of the pyrolytic chars was characterised using a Zeiss$^{@}$ Sigma VP Scanning Electron Microscope with an accelerating voltage of 10 kV. Normally, the working distance was 9.5 cm. Secondary electron detector (SE2) and In-lens detectors were applied for SEM imaging.

3.2.4.4. Energy Dispersive X-Ray Spectroscopy

Elemental composition of the pyrolytic chars was determined by using an Energy Dispersive X-ray Spectroscopy (EDS) via an x-act quantitative silicon drift detector supplied by Oxford Instruments, UK, which is attached to the existing SEM. 20-25 kV was applied to generate adequate X-ray from the sample to reach the EDS detector. For each pyrolytic char sample, 20 points were scanned, and the average of compositions was recorded and calculated.

3.3. Hybrid recycling process

In this experiment, a hybrid recycling process was carried out to particularly reduce or remove the char during the conventional pyrolysis stage. The clean carbon fibre could potentially be recycled in a shorter oxidation duration as this not only reduces energy consumption, but better preserves the mechanical performance of the recycled fibre. The optimized conventional pyrolysis condition of lowest char formation studied in Section 3.2 was applied in the conventional pyrolysis after the chemical pre-treatment process. The effect of chemical pre-treatment on thermal degradation temperature and surface morphology of CF/EP prepreg was investigated. The mechanical properties, surface morphology, surface element and graphitization degree of recovered carbon fibre was analysed. The detailed materials, experiment method and characterization will be introduced in the following section.

3.3.1. Materials

The unidirectional CF/EP prepreg consists of Bisphenol-A epoxy resin (37 wt.%) and Toray@T700s carbon fibres were used in this experiment, and the detailed information has been described in Section 3.2.1.

Other chemicals used in the pre-treatment stage including zinc Chloride ($ZnCl_2$) and Ethanol (C_2H_5OH). $ZnCl_2$ powder (analytical reagent, CAS number: 7646-85-7, purity: 98 %) was used as a solute in the catalytical solution for chemical pre-treatment and was provided by Macklin@ chemical technology co. LTD in Shanghai, China. C_2H_5OH (analytical reagent, CAS number: 64-17-5, purity: 95 %) was used as the solvent in the catalytical system for chemical pre-treatment before pyrolysis and was provided by Hushi@ Lab. Equipment co. LTD in Shanghai, China.

3.3.2. Experimental method

A new hybrid method consists of chemical pre-treatment and conventional pyrolysis was used to recover carbon fibre without extra oxidation. The process flow of the hybrid method is shown in Figure 3-5.

As a comparison, a standard conventional pyrolysis method with extra oxidation was also carried out. The recovered fibre obtained from both methods were characterized and compared with the virgin fibre. The detailed procedures are introduced below.

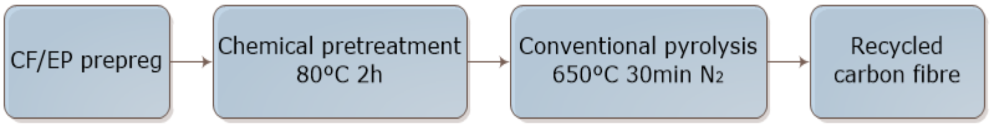


Figure 3-5 The process flow of the hybrid method.

3.3.2.1. Chemical pre-treatment process

In the chemical pre-treatment process, the CE/EP prepreg was immersed in the pre-treatment agent consisting of zinc chloride and ethanol. The experimental set-up is shown in Figure 3-6. The pre-treatment agent was prepared by dissolving $ZnCl_2$ powder (40 wt.%) in 150 ml of ethanol in a beaker and was heated up to 80 °C using a magnetic stirrer. Cured prepreg with the size of 20 mm × 20 mm were immersed in the solution for 2 hours with constant stirring to ensure homogeneous treatment. The top of the beaker was sealed to prevent the solution from evaporation. After the chemical process, the treated sample was washed with distilled water several times, then it was dried in an oven at 80 °C for 24 hours.

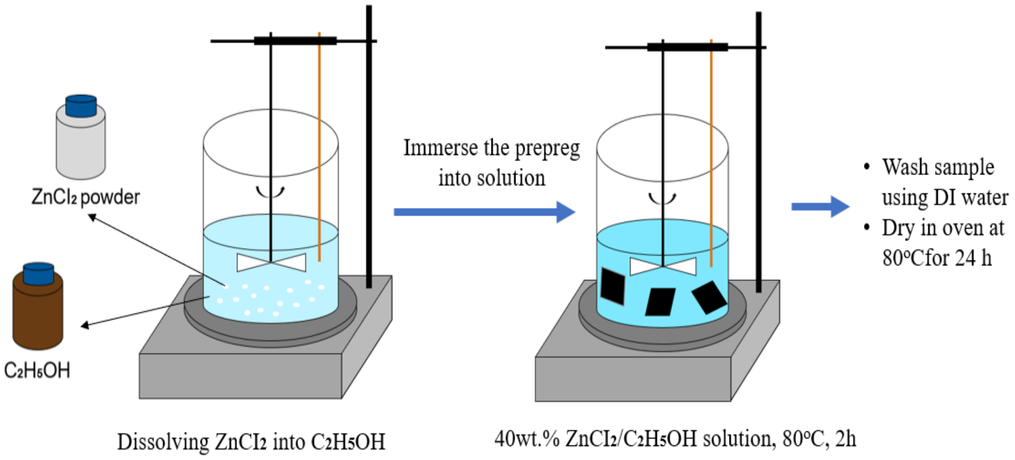


Figure 3-6 The experimental setup of chemical pre-treatment process.

3.3.2.2. Conventional pyrolysis process

To satisfy the investigation of mechanical properties of recycled fibre, the pre-treated sample with the size of 20 mm × 20 mm was pyrolyzed at 650 °C for 30 minutes in a sliding tube furnace (OTF-1200X, shown in Figure 3-7) supplied by Kejing$^{@}$ equipment company, Hefei, China. The sliding tube furnace was selected to achieve a higher heating rate closer to industrial application. 20 g pre-treated sample of CF/EP prepreg in an alumina crucible was placed at the left side of the tube. The furnace was heated in nitrogen gas with a flow rate of 1000 ml/min. When the temperature of the furnace reached at 650 °C, the extra 1200 ml of compressed air was injected to the tube, and finally nitrogen gas purged again. The furnace was slid to the sample position to start the pyrolysis when the temperature steadied at 650 °C. After pyrolysis for 30 minutes, the sample was collected when the furnace cooled to the room temperature in nitrogen.

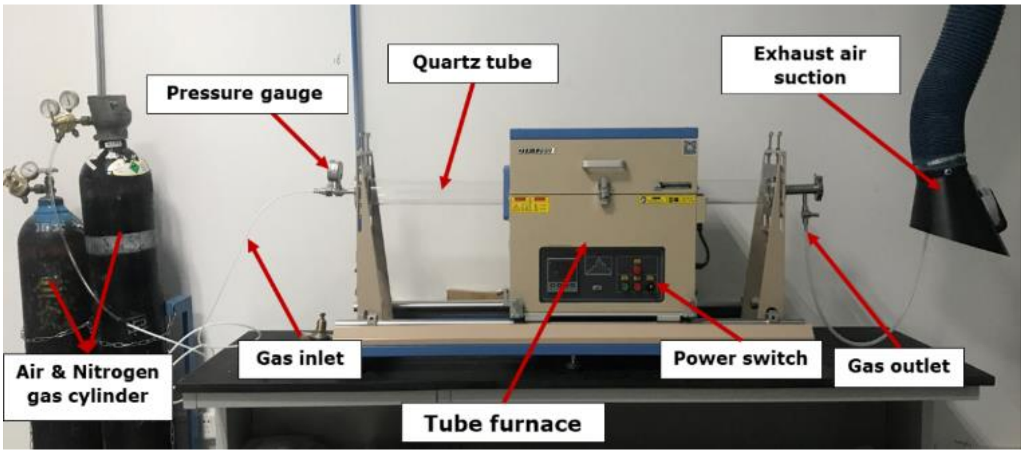


Figure 3-7 The sliding tube furnace.

A standard conventional pyrolysis recycling method with extra oxidation of the as-received prepreg was used to compare with the new hybrid method described above. The process flow of the standard conventional pyrolysis recycling method is shown in Figure 3-8. 20 g the as-received CF/EP prepreg with the size of 20 mm × 20 mm in a square alumina crucible was placed at the left side of the tube furnace. When the temperature reached and steadied at the temperature of 650 °C, the heating unit was slid to the sample position to perform the pyrolysis for 30 min. The extra 1200 ml of compressed air was injected to the tube whilst sliding the heating unit to the sample position. During heating and pyrolysis, 1000 ml/min nitrogen gas was introduced continuously to provide the inert gas atmosphere. After pyrolysis, compressed air with the flow rate of 1000 ml/min was provided to oxidise the pyrolytic char at the same temperature for 30 minutes.

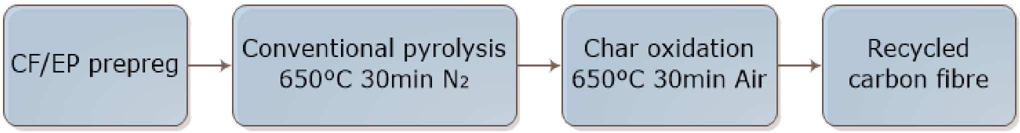


Figure 3-8 The process of standard conventional pyrolysis recycling method.

3.3.3. Characterizations of carbon fibre epoxy prepreg

Characterizations were focused on pre-treated CF/EP prepreg and the as- received prepreg to evaluate the effect of pre-treatment on the degradation behaviour and surface properties of prepregs.

3.3.3.1. Thermogravimetric analysis

A TGA (Figure 3-2) was used to establish the effectiveness of the pre-treatment process by comparing the degradation profiles of the treated specimens against a control unit, which had not been pre-treated. After the pre-treatment process, 20 mg dried CF/EP prepreg with a size of 5 mm × 4 mm was placed in a small alumina crucible for pyrolysis. The sample was heated to 650 °C with a heating rate of 200 °C/min and was held isothermally for 30 minutes. 120 ml compressed air was first injected to the furnace before starting the heating process, then a nitrogen gas flow rate of 50 ml/min was introduced for both of the heating and isothermal stages. The as-received prepreg was also pyrolyzed in the same condition for benchmarking, and the mass loss of treated prepreg and as-received prepreg were analyzed.

3.3.3.2. Surface electron microscopy

The CF/EP prepreg before and after pre-treatment were characterized using an SEM mentioned in Section 3.2.4.3 with an accelerating voltage of 20 kV to evaluate the degradation effect of chemical pre-treatment process on the surface of prepregs. The operating accelerating voltage was 10 kV and the working distance was 9.5-10 mm. Secondary electron detector (SE2) and In-lens detectors were applied for SEM imaging.

3.3.3.3. Energy Dispersive X-Ray Spectroscopy

To study the effect of chemical pre-treatment on the surface elemental composition of CF/EP prepreg, Energy Dispersive X-ray Spectroscopy (EDS) attached to the SEM described in Section 3.2.4.3 were used using the voltage of 20-25 kV. The major element of carbon (C), oxygen (O), zinc (Zn) and chloride (Cl) were scanned. For each sample, three square areas were scanned, and the average of compositions was recorded and calculated.

3.3.4. Characterizations of recycled carbon fibre

Recycled carbon fibre collected from both hybrid recycling method and standard conventional pyrolysis were characterized to evaluate the quality of fibre. The detailed methods are described in the following sections.

3.3.4.1. Single fibre tensile test

The tensile strength and modulus of virgin and recycled carbon fibre were determined using a single fibre tensile tester (DiaStron@ LEX810/820, UK) and conducted following ISO 11566 Carbon fibre tensile properties determination standard. A LEX820 module was used to compute stress/strain data and an LDS0200 module for diameter measurements using laser diffraction. The single fibre tensile tester and main test modules are shown in Figure 3-9 and Figure 3-10. The individual fibres were fixed with the dual-ended mounting tabs using UV cured epoxy glue and then positioned on a steel sample tray (Figure 3-11). For each test condition, 30 individual fibres were tested with the gauge length of 4 mm and load cell of 1 N. A constant strain of 0.1 mm/s was applied, and the stress/strain curves of the mounted fibres were recorded automatically to calculate the tensile strengths and modulus.

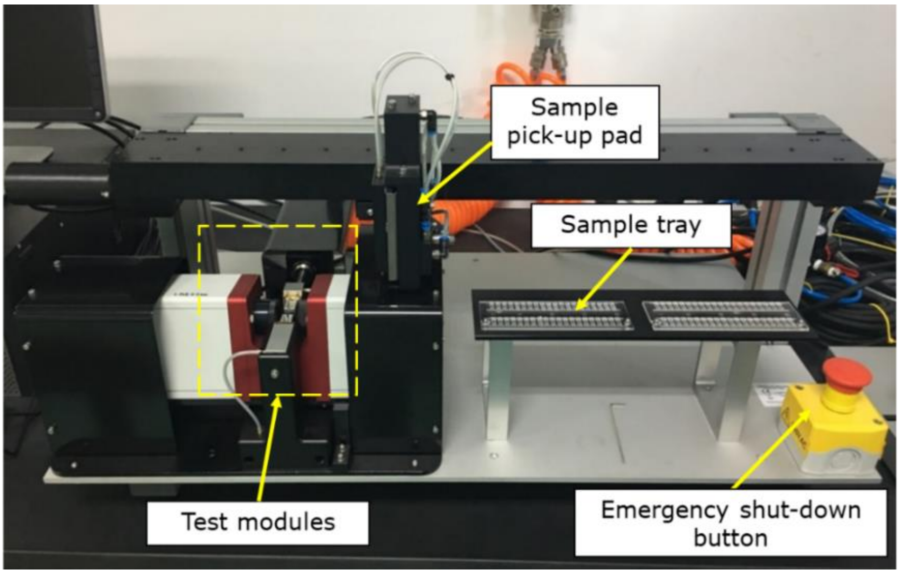


Figure 3-9 Single fibre tensile tester.

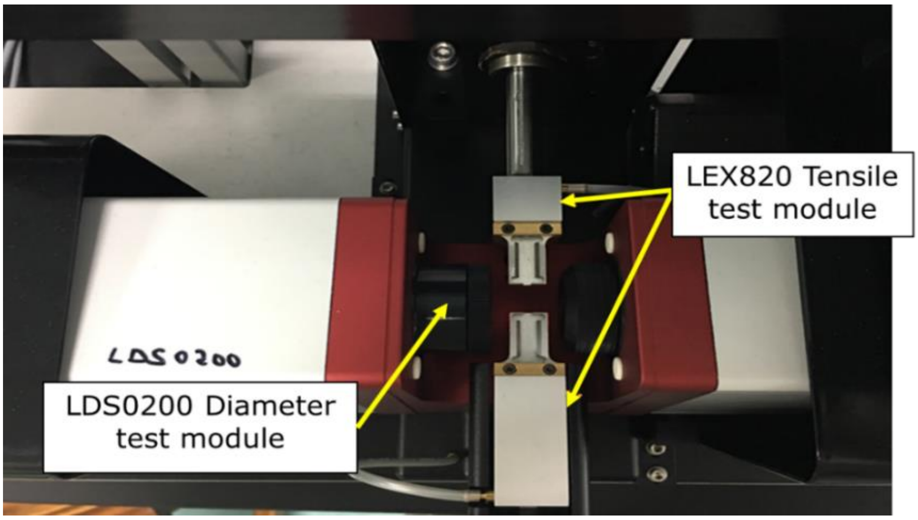


Figure 3-10 The main test part of single fibre tester

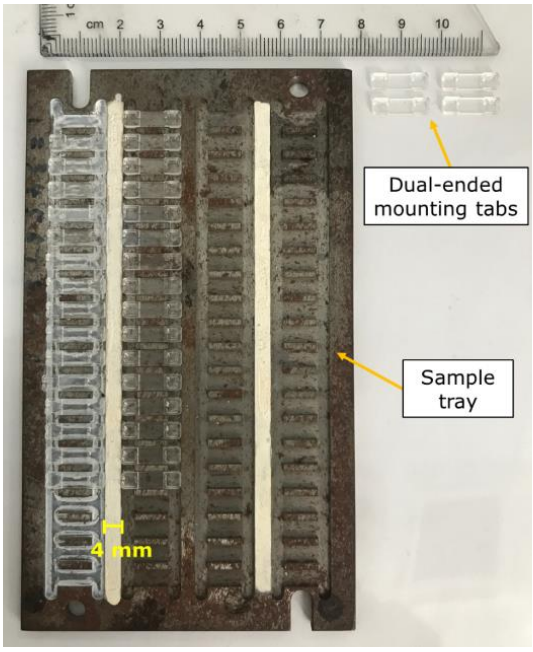


Figure 3-11 Steel sample tray (Gauge Length=4mm).

3.3.4.2. X-ray photoelectron spectroscopy

The surface element and functional group of virgin and recycled carbon fibre were determined using X-ray photoelectron spectrometer (XPS, AXIS ULTRA DLD, Shimadzu, Japan) with an Al Kα X-ray source (1486.6 eV) at a power of 15 kV and 450 W. The wide scan spectra with a step of 1 eV and high resolution spectra with the step of 0.05 eV were recorded in the range of 0–1200 eV. Surface atomic composition and curve-fitting of the XPS spectrum were analysed using CasaXPS software package. The carbon (C), hydrogen (H), oxygen (O), nitrogen (N), zinc (Zn) and chlorine (Cl) traces were scanned. The binding energy was calibrated by referring to the C 1s peak at 284.8 eV (Cai et al., 2019).

3.3.4.3. Raman spectroscopy

Raman spectroscopy is a useful approach to analyze amorphous, crystalline and non-crystalline phases of carbon materials. Raman spectroscopy was used to investigate the degree of graphitization of recycled carbon fibres. Raman spectra were obtained at room temperature using an inVia-Reflex Raman spectrometer (Renishaw, Gloucestershire, UK) with a 532 nm laser diode. The scanning wavenumber was in the range of 800 cm^{-1} to 2200 cm^{-1}. The spectra of virgin and recycled carbon fibre were obtained and then analysed using the Origin software.

3.3.4.4. Surface electron microscopy

The surface morphology of both virgin and recycled carbon fibre were observed using a scanning electron microscope (ZEISS@ Sigma VP) to investigate the degree of degradation of the resin matrix and potential damage to the fibre surfaces (D.Akesson and M.Skrifvars, 2011). The operating accelerating voltage was 10 kV and the working distance was 9.5-10 mm. Secondary electron detector (SE2) and In-lens detectors were applied for SEM imaging.

3.4. Microwave pyrolysis process

In this experiment, carbon fibre was extracted from carbon fibre prepreg using microwave pyrolysis at different temperatures. The mechanical properties, surface morphology, surface element of recovered fibres were analysed. The component and composition of pyrolytic gas and oil were investigated. The detailed materials and experimental method will be described below.

3.4.1. Materials

The unidirectional CF/EP prepreg consists of Bisphenol-A type epoxy resin (37 wt.%) and Toray@T700s carbon fibres were used in this experiment, and the detailed information has been described in Section 3.2.1.

Other chemical involved dichloromethane (CH_2Cl_2, Sino Reagent, CAS number: 75-09-2, purity: 99.99 %), which was used as a solvent in the condensation section for the collection of pyrolytic oil. Another CH_2Cl_2 (Sigma, CHROMASOLV$^{@}$ Plus grade) was also employed as a solvent for gas chromatograph-mass spectrometry (GC-MS) analysis. An Ultra Light-Weld 3193 adhesive supplied by DYMAX$^{@}$, USA was used to stick the individual fibre with the tabs of single fibre tensile tester described in Section 3.3.4.1. The adhesive was cured using the UV Light and the detailed test method was described in Section 3.3.4.1.

3.4.2. Experimental method

Microwave pyrolysis of cured carbon fibre reinforced epoxy prepreg (CF/EP) was carried out in a 2.45 GHz multi-mode microwave cavity (Nanjing Jiequan Microwave Co., Ltd., China, as shown in Figure 3-12) with the maximum microwave power of 3 kW. A customized high-temperature resistance and microwave transparent vertical glass tube (available diameters are 50 mm, 100 mm and 200 mm) was used as a holder to place the material and conduct the pyrolysis reaction (shown in Figure 3-13). To improve the heating uniformity, the microwave reactor was modified to rotate the glass tube, the operating rotational speed was 20 rpm. The material was heated via two 1.5 kW magnetrons. There are 2 types of control mode, which are the temperature control mode and power control mode. The operating temperature was determined by using an insulated K-type thermocouple (time constant<10 s) positioned at the centre of the tube reactor, the temperature measuring range of which was 0-1500 °C. A temperature control mode was chosen so that the temperatures of sample were constantly maintained at a target temperature after an initial temperature ramping.

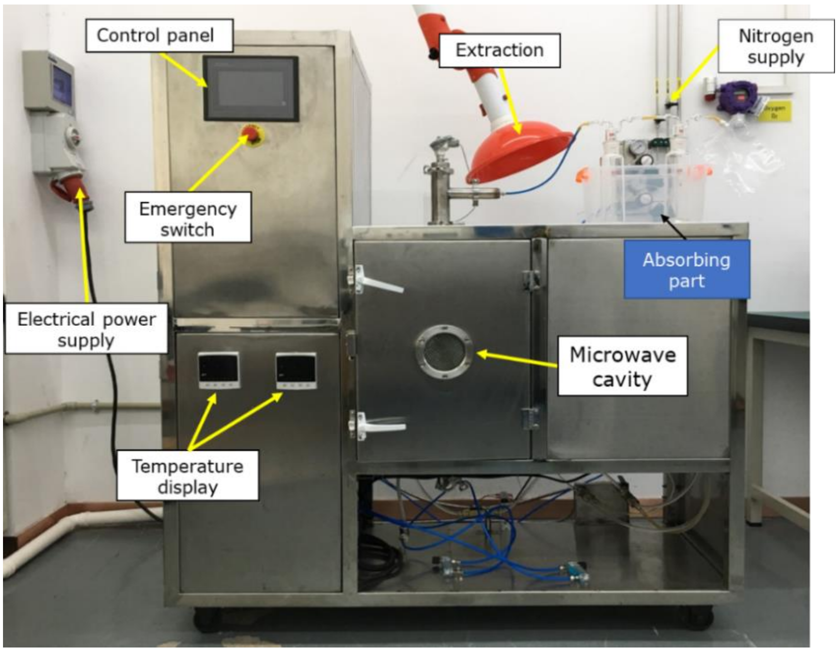


Figure 3-12 Multi-mode microwave rig.

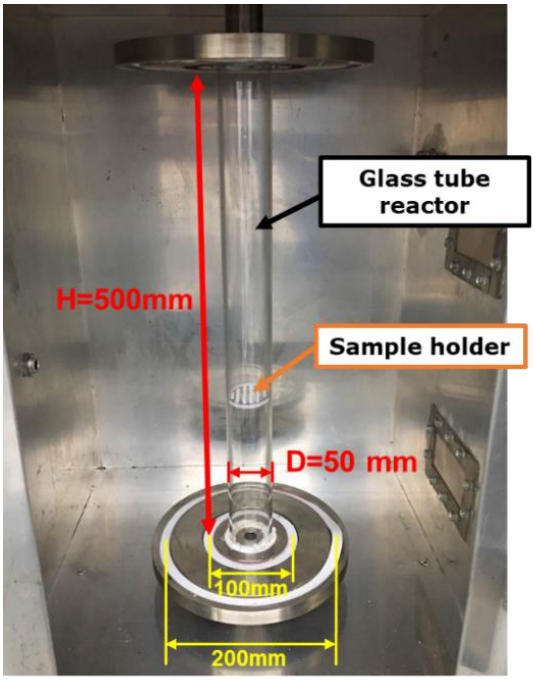


Figure 3-13 Glass tube reactor in the microwave cavity.

The setup of the microwave pyrolysis system is depicted in Figure 3-14. For each test, 20 g CF/EP prepregs trimmed to 100 mm × 50 mm (100 mm along the fibre axis) was inserted into the inner glass tube reactor (tube diameter = 50 mm) and then was heated to the chamber temperature of 450 °C, 550 °C and 650 °C for 15 min. The temperature of prepregs was measured using the K-type thermocouple. The microwave power was switched off automatically when the temperature reached the pre-set temperature. The target temperature was selected in accordance with prepreg thermal behaviour tests. A nitrogen gas flow rate of 100 ml/min was purged into the reactor 10 minutes before and during the experiment to provide the inert gas environment and carry the pyrolyzed gas out of the reactor. The downstream gas was collected in an absorbing part. The condensable volatiles were dissolved using dichloromethane in the ice bath, whilst the rest of the gas product was collected using gas bags. After microwave pyrolysis, the residual solids (fibres and char) inside the glass tube reactor were collected using ceramic crucibles and heated in air at 550 °C for 30 min using an atmospheric furnace (KSL-1200X, Kejing® Ltd., Hefei, China). After oxidation, the obtained fibres were collected and underwent further testing. The experimental schemes are summarized in Table 3-1.

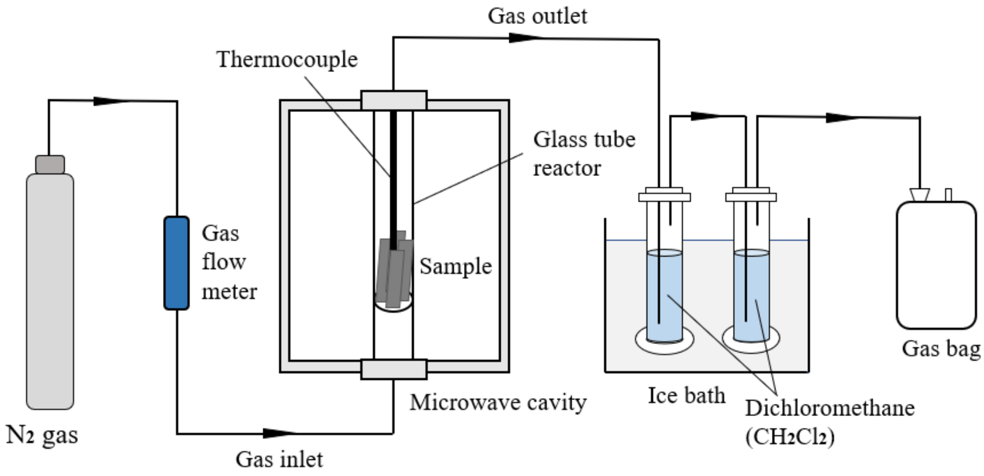


Figure 3-14 The experimental setup for the microwave pyrolysis system.

Table 3-1 Experiment summary of microwave pyrolysis and oxidation

Material	Microwave Pyrolysis		Thermal Oxidation	
	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)
CF/EP prepreg	450	15	550	30
	550	15	550	30
	650	15	550	30

3.4.3. Pyrolytic products characterizations

After microwave pyrolysis, the main pyrolytic products were solid residue (fibre and char), pyrolytic gas and pyrolytic oil. The pyrolytic product yield was calculated. The recycled carbon fibres were characterized and the virgin carbon fibre was also included as the benchmark. The components and composition of pyrolytic gas and oil were also investigated. The detailed method will be introduced below.

3.4.3.1. Thermogravimetric analysis

A non-isothermal test was carried out in a TGA (shown in Figure 3-2) from room temperature to 1100 °C with a heating rate of 10 °C/min to determine the thermal degradation behaviour of carbon fibre prepreg under nitrogen and air. The devolatilised temperature of carbon fibre prepreg was determined from the mass loss curve (TG) and the first derivative of the mass loss curve (DTG) in heating nitrogen. The oxidation behaviour and temperature of carbon fibre prepregs were analysed from TG curve and DTG curve heating in air.

3.4.3.2. Pyrolytic product yield analysis

The solid pyrolysis product yield was determined from the mass of solid residue inside the glass tube reactor. The liquid product consisted of oils absorbed by the two gas-washing bottles and that remaining on the inside of the glass tube reactor. The oils were collected by evaporating the dichloromethane in a fume hood. The yield of liquid product was determined from the total mass of oil collected. The assumed gas product yield was estimated from the difference in resin weight percentage with solid and oil product yield.

3.4.3.3. Single fibre tensile test

The tensile strength and modulus of virgin and recycled carbo fibre were determined using the single fibre tensile tester. The detailed test method was described in Section 3.3.4.1 For each test, 30 single fibres were tested, and the data were analysed using Weibull distribution.

3.4.3.4. Surface electron microscopy

SEM was performed on both fibre recycled form pyrolysis with pre-treatment and with oxidation. The virgin fibre was also included. The detailed method was described in Section 3.4.3.4.

3.4.3.5. X-ray photoelectron spectroscopy

The surface element and functional group of recycled carbon fibre from pyrolysis with chemical pre-treatment and with oxidation were determined using XPS. The detailed test method was described in Section 3.4.3.4. The carbon(C), hydrogen (H), oxygen (O) and nitrogen (N) element were scanned.

3.4.3.6. Gas chromatography

The composition of the pyrolytic gas product was determined using a gas chromatograph (GC, Shimadzu GC-2014, Japan), which was equipped with 1 Flame Ionization Detector (FID), 2 Thermal Conductivity Detector (TCD), 8 molecular sieve columns and 1 HP-AL/s capillary column. The injection temperature, column temperature and detector temperature were set at 60 °C, 200 °C and 170 °C, respectively. Air, hydrogen and nitrogen were used as carrier gas. The system GC is capable of separating C_1-C_5 hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, C_4H_6, i-C_5H_{12} and n-C_5H_{12}, etc.) and permanent gas (O_2, N_2, H_2, CO, CH_4, and CO_2, etc.) simultaneously; meanwhile their volume contents can also be determined using the external standard method.

3.4.3.7. Gas chromatography-mass spectrometry

The composition of the pyrolytic oil was determined using a gas chromatograph-mass spectrometry (GC-MS, Agilent 7890-5975C, USA). The oven temperature was then increased to 280 °C with heating rate of 10 °C/min, and then held this temperature for 2 minutes. An HP-5 ms capillary column (Length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm) was used. The initial oven temperature of the GC was kept at 60 °C for 2 minutes. The chromatograph was equipped with a split/splitless injector used in the split mode. The split ratio was 50:1. The chromatogram peaks were identified by comparing their mass spectra with NIST 2011 library database.

Chapter 4. Optimization of conventional pyrolysis

4.1. Introduction

Due to the lack of research which focuses on the optimization of conventional pyrolysis in reducing or removing char of the recovered carbon fibre, various pyrolysis conditions were applied to investigate the optimum pyrolysis parameter. The literature shows that three parameters, heating rate, temperature, and gas flow rates, are considered the key factors to affect the pyrolysis. In this chapter, a description is given of the different pyrolytic conditions i.e., heating rates, temperatures and nitrogen gas flow rates, which were applied for carbon fibre epoxy (CF/EP) prepreg and carbon fibre phenolic (CF/PF) prepreg. A thermogravimetric analyser was used to study the char formation and oxidation rate of char derived from the two different thermoset resins. Then, the chars were subjected to the intrinsic reactivity analysis via TGA (Section 4.4.1), elemental composition via EDS (Section 4.4.2), surface area and pore size via BET analysis (Section 4.4.3) and morphology study via SEM (Section 4.4.4).

4.2. Effects of heating rates and pyrolysis temperatures on char formations

Thermogravimetric analysis was implemented to incur a pyrolysis reaction on prepreg in order to study the effects of heating rates and pyrolysis temperatures on its thermal degradation property, particularly the amount of char generated from the resin matrix under a nitrogen-filled environment. The detailed method of this analysis has been described in Section 3.2.2. Since the carbon fibre was stable during pyrolysis, the weight change of corresponded thermoset resin in the CF/EP prepreg and CF/PF prepregs in an inert environment under various heating rates and pyrolysis temperatures are presented in 错误!未找到引用源。 (a) and (b). It can be seen a distinct difference in mass loss profiles between them. For the epoxy in CF/EP prepreg, a marginal mass loss is first observed due to dehydration, then devolatilization of epoxy matrix caused a significant decrease in mass and finally a steady state is reached. This trend is observed from each curve shown in 错误!未找到引用源。(a). Whilst for the phenolic in CF/PF prepreg, as shown in 错误!未找到引用源。(b), three degradation stages are evident, particularly from the tests with the slowest heating rate of 20 °C/min, which begin with dehydration and formation of additional intermolecular crosslinks via condensation reactions at temperature up to around 200 °C (Chen et al., 2008b; Pimenta and Pinho, 2011), then at higher temperatures, the crosslinks are broken, releasing volatiles such as phenol, aldehyde, water and short oligomers (Zhao et al., 2013) and finally the last stage with temperature above 400 °C, which involves mainly release of hydrogen gas and it accounts for the main mass drop in this material (Chen et al., 2008b; Trick and Saliba, 1995). It is also noticed that unlike the epoxy resin in CF/EP prepreg which shows a fair plateau region at the end of the pyrolytic test, a steady decrement in mass was observed from the phenolic resin in CF/PF prepregs, suggesting the final dehydrogenation and char carbonation are both temperature and time dependent.

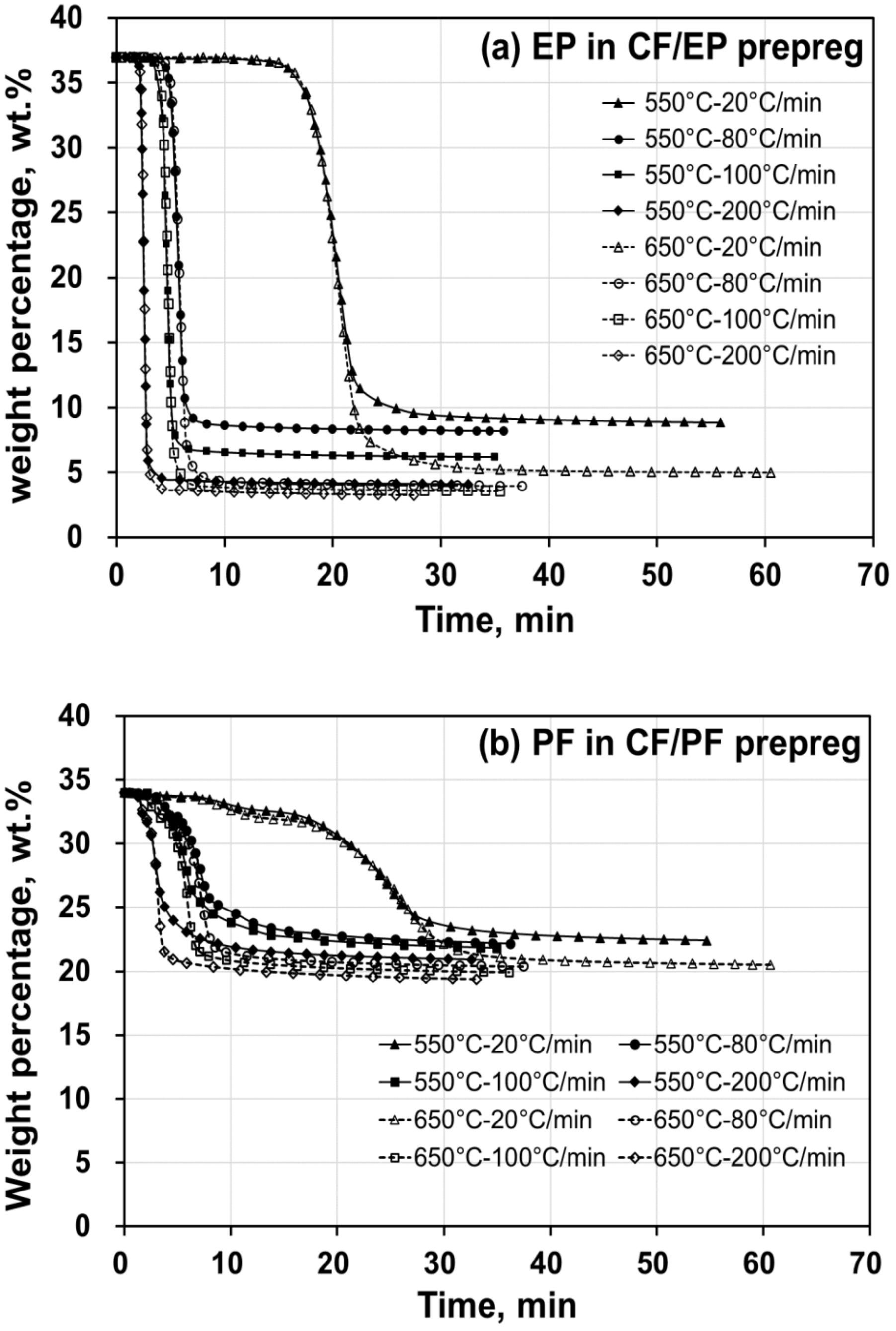


Figure 4-1 Weight change curve of (a) epoxy resin in CF/EP prepreg and (b) phenolic resin in CF/PF prepreg pyrolyzed at different heating rates and pyrolysis temperatures, as a function of time.

Since pyrolysis treatment hardly affects the carbon fibre, the differences in the final mass shown in 错误!未找到引用源。are attributed to the degree of char retention. The net amounts of char attained after 30 minutes of isotherm period were determined by subtracting the corresponding carbon fibre content from the final mass values and these data are plotted in Figure 4-2 as a function of heating rate at two different pyrolysis temperatures. Typically phenolic has higher flame resistance than epoxy resin (Hshieh and Beeson, 1997) because of its three-dimensional crosslinked network containing phenol molecules and methylene, which promotes high char yield (Wang et al., 2017). This is observed in Figure 4-2 with char contents found from the CF/PF prepreg are much higher. Whilst CF/EP prepreg had much lower char content, probably because of high secondary cracking, which converted large proportion of epoxy into volatiles, such as hydrogen, methane, carbon monoxide and carbon dioxide (Naqvi et al., 2018). It can be seen that the char contents of both CF/EP and CF/PF prepregs are dependent on heating rate. At the slow heating rate, the char contents are higher but decreasing steadily until the heating rate is higher than 100 °C/min before approaching an asymptotic value. The amount of heat energy available for efficient heat transfer to the interior of samples is controlled by heating rate and this influences the rate of devolatilisation (Seung-Soo et al., 2013). At a low heating rate, it takes a longer time to reach pyrolysis temperature and this prolonged residence period favours secondary reactions, for example, cracking, re-polymerization and re-condensation in the released volatiles, leading to a higher char residue content (Maiti et al., 2007). Similar effect on char reduction was also reported by Pei et al. (Pei et al., 2013) from their pyrolysis study on thermoplastic plastic wastes, such as PE, PP and PVC, in conjunction with other reports on biomass materials, such as Crofton weeds (Cheng et al., 2019) and alligator weeds (Bhattacharjee and Biswas, 2018).

Figure 4-2 also shows that at a higher temperature of 650 °C, a lower char content can be further attained and this applies for both of the CF/EP and CF/PF prepregs, due to availability of more thermal energy to breakdown stronger organic bonds in the matrices (Zhang et al., 2016). Similar results were obtained from pyrolysis studies on large particle coal (Valdés and Chejne, 2018), wood (Zeng et al., 2015b), and municipal solid waste (Anh et al., 2008). In this context, higher heating rate and pyrolysis temperature both led to a lower char residue on the recovered carbon fibre surface.

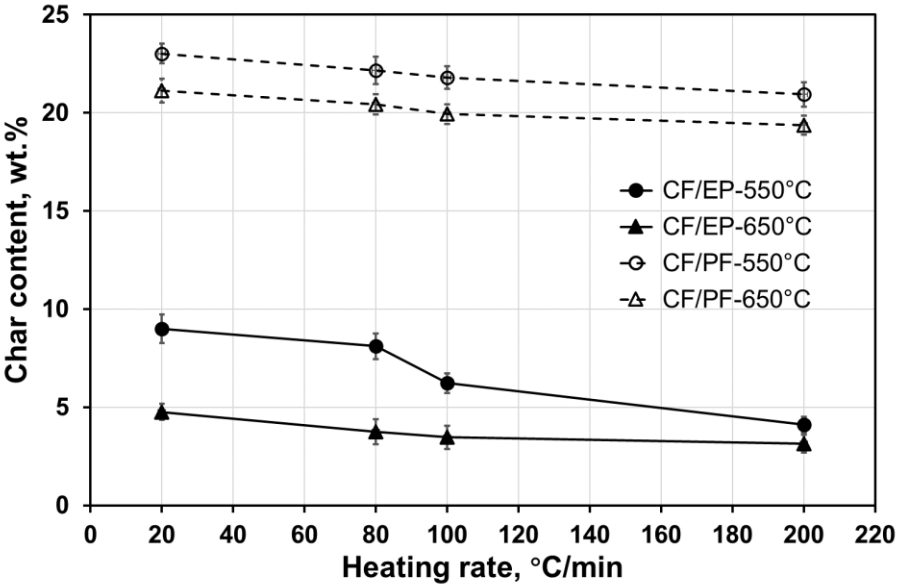


Figure 4-2 The char content of CF/EP prepreg and CF/PF prepreg after pyrolyzed at different heating rates and temperatures.

4.3. Effect of nitrogen gas flowrates on char formations

Figure 4-3 shows the effect of nitrogen gas flow rate on char content obtained from CF/EP prepreg and CF/PF prepreg after pyrolysis tests under different heating rates and pyrolysis temperatures. Nitrogen gas stream not only maintains an inert pyrolysis environment but also removes volatiles from the degrading prepregs. Short residence time for the volatiles can reduce secondary reactions (Cheng et al., 2019), such as cracking of volatiles and re-polymerization in hot charred particle, which lead to a lower char yield (Açıkalın and Karaca, 2017; Lanzetta et al.) and this was the reason for reducing char mass observed on CF/EP prepreg. It is important to mention that this desirable effect became insignificant when the heating rate was higher than 100 °C/min, as it can be seen from Figure 4-3 (a) that the char balance remained at around 4 wt.%, independent of gas flow rate. Thus, a higher flow rate was not required for suppressing the suggested secondary reactions for cases with high heating rate. This implied that volatiles residence time can be influenced not only by the purging gas flow rate but also the heating rate. Similar conclusions were reached by Montoya et al. (2015) and Haykiri-Acma et al. (2006). Both attributed higher heating rates to the reduction in char residues. For the CF/PF prepreg, as shown in Figure 4-3 (a), a weaker but similar relationship between char content and nitrogen gas flow rate is observed for heating rate less than 100 °C/min. Above 100 °C/min, the char content stayed at around 20.5 wt.%.

Figure 4-3 (b) shows the effect of gas flow rate on char residues derived from CF/EP and CF/PF prepregs at 650 °C. It can be seen that a rather complex relation between gas flow rate and devolatilization process is observed. For the CF/EP prepreg, a general trend toward lower char content with increasing flow rates can be identified for heating rates less than 200 °C /min. However, at lower heating rates of 20 and

80 °C/min, the trend only applied for increasing the gas flow rate up to 200 ml/min, beyond which, an increase in char contents is found. For the CF/PF prepreg, a slight decrease in char content can be seen with increasing the flow rates, regardless of heating rates and pyrolysis temperatures. This relatively weak effect of flow rate on the decrease in char content indicated that the aforementioned secondary reactions did not apply for the CF/PF prepreg and the chars created from the CF/PF prepreg were thermally stable. It has been reported by Jiang et al. (2012) that methylene scission was the main reaction for the decomposition of phenolic resin, which was gradually transformed into amorphous char through a polycyclic aromatization. The degree of methylene scission between phenolic groups had a direct contribution to char yield (Alonso et al., 2011), suggesting the charring phenomenon is less influenced by the volatiles' residence time inside the chamber, but more on the chemical and crosslinking density of the molecular structure of the phenolic resin.

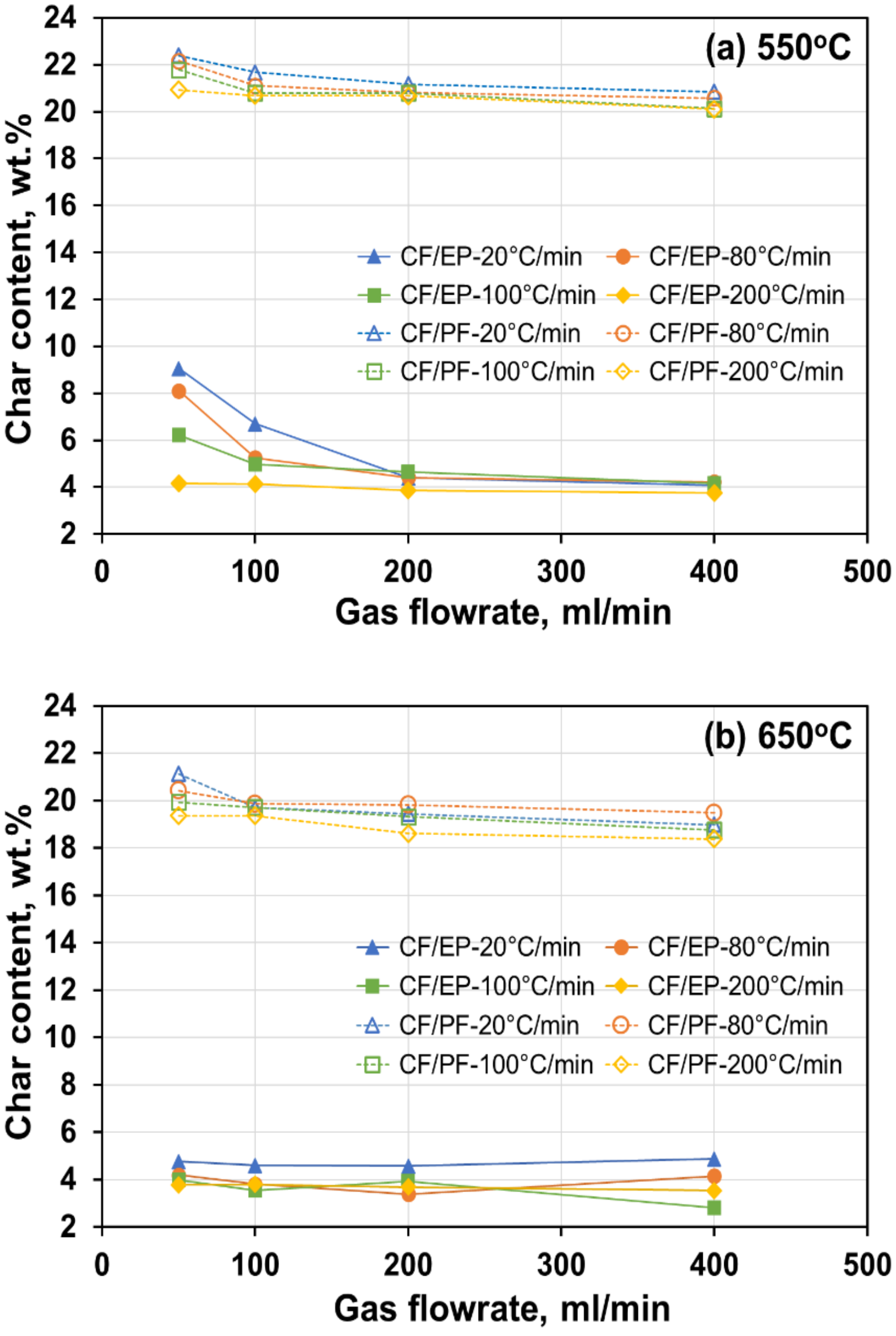


Figure 4-3 Effect of nitrogen gas flow rates on char content obtained from CF/EP prepreg and CF/PF prepreg at (a) 550 °C and (b) 650 °C pyrolysis temperature and different heating rates.

4.4. Characterisation of pyrolytic chars

Neat epoxy and phenolic resins were extracted from the as-received prepregs and they were subjected to the same pyrolysis treatments to be converted into chars for further characterisation, particularly for oxidation study. Oxidative treatment is a necessary process for char residues removal (Meyer et al., 2007) as it directly affects the efficient reuse of carbon fibre recovered from thermoset composite waste. Presence of char residues affect dispersion quality of the recovered fibre in nonwoven and aligned mat making processes (Wong et al., 2010; Wong et al., 2012) and compromises resin impregnation in subsequent moulding step, which can potentially impair interfacial adhesion strength between the fibre and new resin matrix. However, as both carbon fibre and char are primarily carbonaceous materials, both are oxidised at the same time at high temperature, making it difficult to solely focus on char oxidation behaviour investigation. In this study, the extracted neat resins were pyrolyzed using the same range of heating rates and pyrolysis temperatures as the prepregs, to create chars, which were free of carbon fibre.

4.4.1. Intrinsic reactivity analysis

Figure 4-4 shows the results obtained from the non-isothermal intrinsic reactivity analysis on combustion behaviour of chars derived from the neat phenolic resin, together with data obtained from the neat epoxy resin. Intrinsic reactivity defines solely the rate of the chemical reaction between the internal surface of char and an oxidising gas, with exclusion of mass transfer or pore diffusion limitations (Barranco et al., 2003). A char with a high intrinsic reactivity can be oxidised quicker and this is indicated by its low peak temperature (PT) and burnout temperature (BT), which can be determined from the non-isothermal test. According to Figure 4-4, it can be observed that, for the EP chars, their PT and BT values are reduced with higher heating rates and this indicates their intrinsic reactivity had been enhanced. PF chars also show the similar trend, but only at heating rates up to 100 °C/min, beyond which a plateau is reached and also in general, the PF chars exhibit a higher BT than that of EP chars, suggesting a higher temperature or a longer process time is required for PF chars removal through oxidisation. It is worth pointing out that a substantial 40 °C drop in BT had been achieved in both EP and PF chars by opting for high heating rate option in pyrolysis and this could be beneficial for preservation of mechanical performance of recovered carbon fibres, which can be degraded in an oxidative environment at high temperature. However, the char intrinsic reactivity was reduced with higher pyrolysis temperature, as indicated by the rise in BT values and this applied for both EP and PF chars. It is further noticed that such rise became less significant for the EP char when a heating rate of 200 °C/min was used. The negative correlation between intrinsic reactivity and pyrolysis temperature well compares with previously reported findings, for example, more nonreactive chars were produced from flax straw when pyrolysis temperature was decreased from 500 °C to 300 °C, due to the formation of more highly ordered structure (Valdes et al., 2018). Zeng et al. (2015c) also confirmed that the ordered structure, due to partial graphitisation at higher pyrolysis temperature, could also be increased with slower heat rates. Benefits of higher heating rate to increase char reactivity had also been reported by Rybak (1988) and Manyà et al. (2015).

The results presented in the current work represents a significant improvement because it demonstrates that with an optimised process window not only reduces char yield but also producing chars which can be oxidised at a lower temperature. So far, such improvement has been attributed to the pyrolytic reaction conditions on char's reactivity, and the change in reactivity had been recognised through the char structural evolution. Indeed, four potential factors leading up to reactivity changed had been proposed by Ashu et al. (1978), such as the presence of high concentration of heteroatoms, high concentration of active carbon sites, better accessibility by gaseous reactants to the active sites and catalytic reaction arising from inorganic impurities in the char. The last factor is ruled out as no catalyst was introduced to both of the pyrolysis and oxidation processes undertaken in this study. However, the suggested three other factors were exploited to provide a better insight into char composition, structure and morphology, leading up to the change in reactivity.

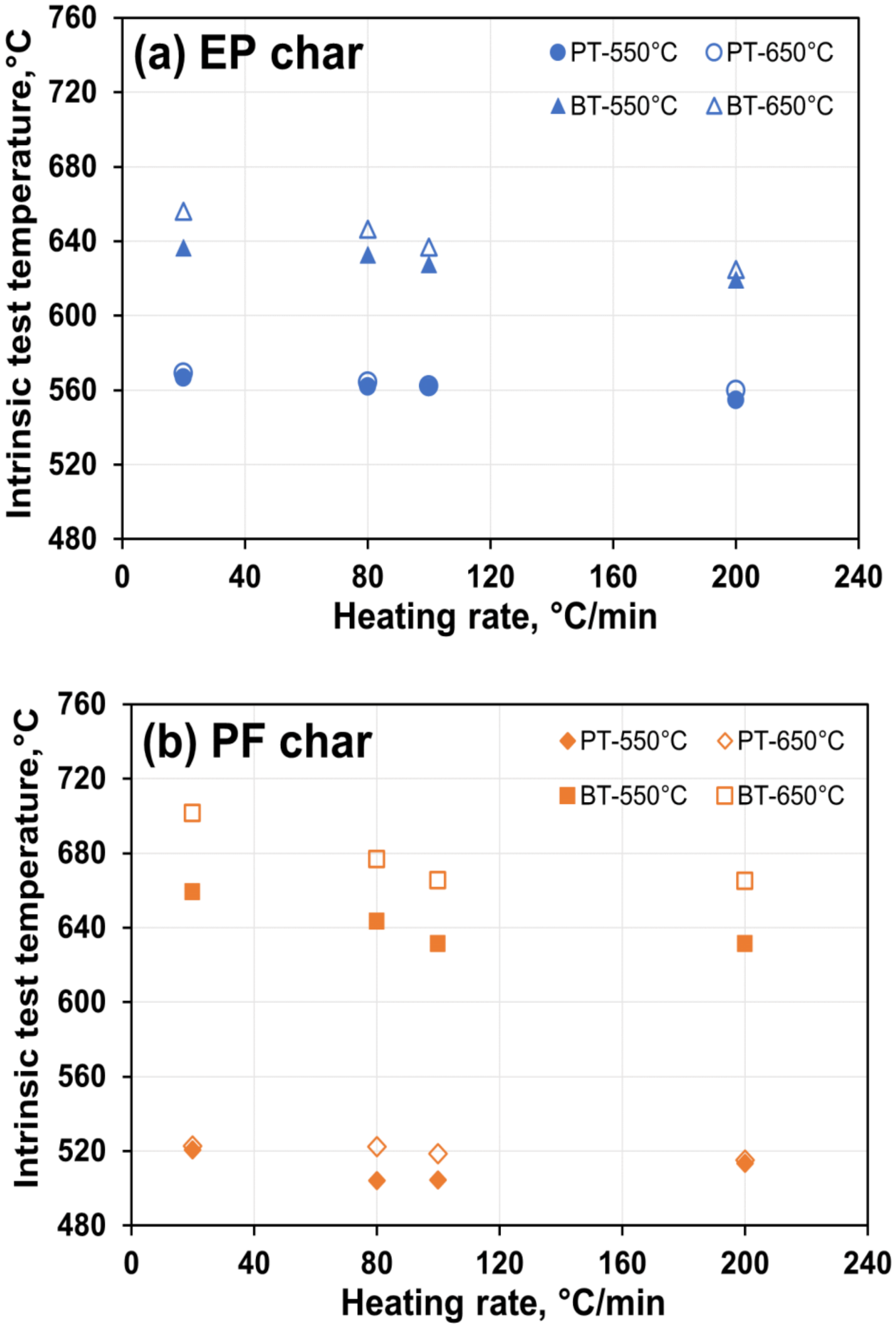


Figure 4-4 Effects of heating rates and pyrolysis temperatures on intrinsic reactivity of chars generated from neat (a) EP and (b) PF resins (PT-Peak Temperature, BT-Burn-out Temperature).

4.4.2. Char elemental analysis

Elemental analysis of pyrolytic chars was determined by an SEM/EDS test and results are presented in Figure 4-5 (a) for the EP char and Figure 4-5 (b) for the PF char. It is noted that for both materials, the carbon and oxygen percentages are both affected by the heating rate. Considerable amount of oxygen element, nearly 30 at.%, was detected from the surface of EP char, especially at the highest heating rate of 200 °C/min, as the oxygen content was more than twice from those with the slowest heating rates. For the EP char, a steady but contradictory change to the atomic carbon and oxygen percentages were registered when the heating rate was increased from 20 °C/min to 100 °C/min. Above 100 °C/min, the effects became more significant. This synergy effects resulted in a continuous rise in oxygen-to-carbon (O/C) ratio, which indicates more oxygen-containing functional groups were found on the char surface with higher heating rates (Yip et al., 2002). The heating rate effect on the change to the carbon and oxygen contents of PF char was not as significant as that of EP char. The carbon percentage decreased slightly with the increment of heating rates whilst the oxygen percentage stayed nearly unchanged, making the O/C ratio grew only gradually with the heating rate. Liu et al. (2020) reported a similar variation in the effect of heating rate on carbon and oxygen element contents of coal char. It is also noticed that the O/C ratio reduced with the use of a higher pyrolysis temperature for both EP char and PF char, which is assumed to the graphitization of carbon structure at high temperature (Zeng et al., 2015a). The O/C ratio of PF char was much lower than that of EP char, due to further condensation of the remaining high-molecular-weight aromatic material to form high yields of char for PF resin (Branca and Blasi, 2013). As reported by Ashu et al. (1978), high concentration of heteroatoms, such as oxygen, increased char intrinsic reactivity, and this echoes with the results shown in Figure 4-4 and Figure 4-5, namely char with highest intrinsic reactivity has the soaring atomic oxygen content.

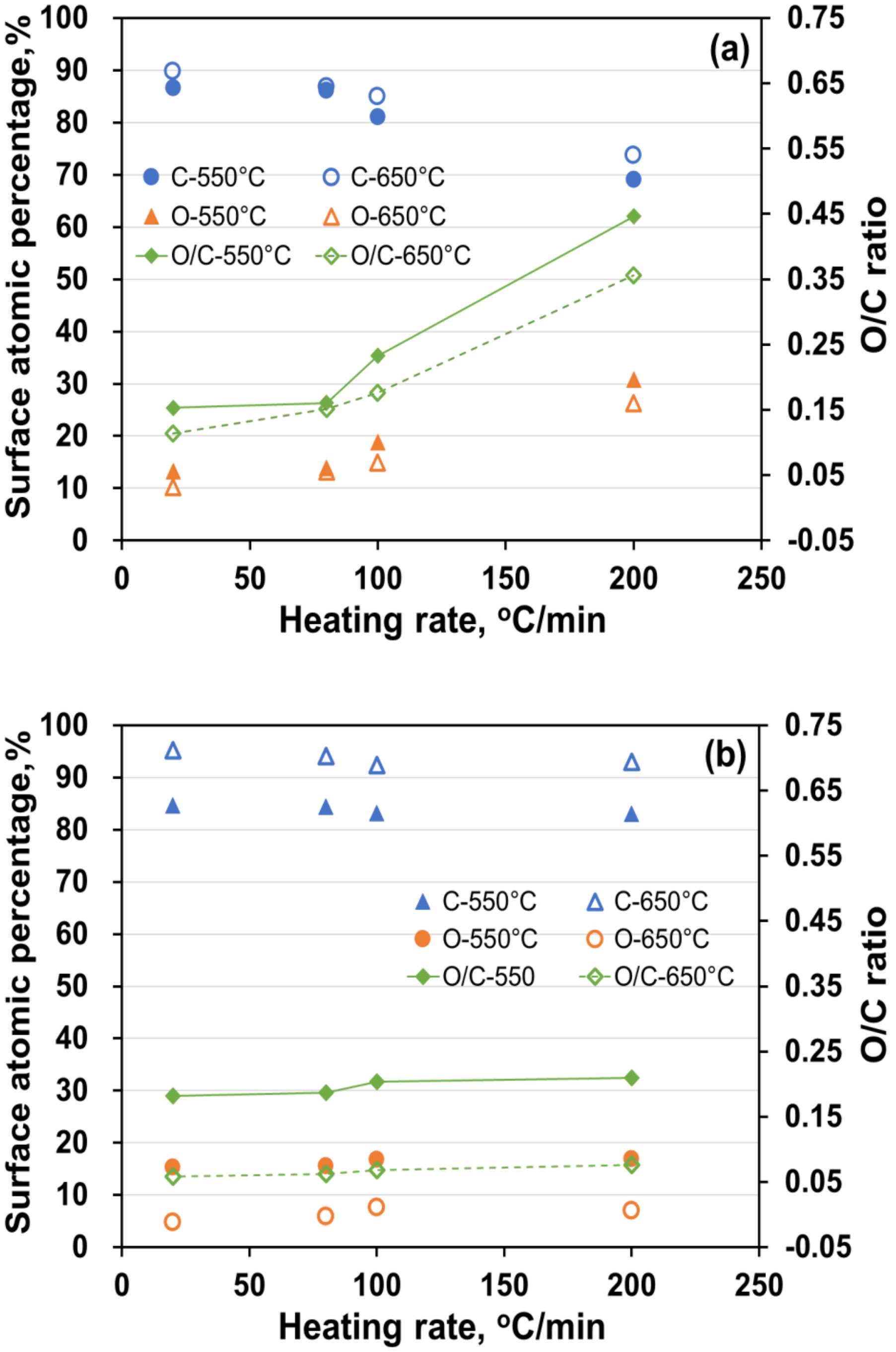
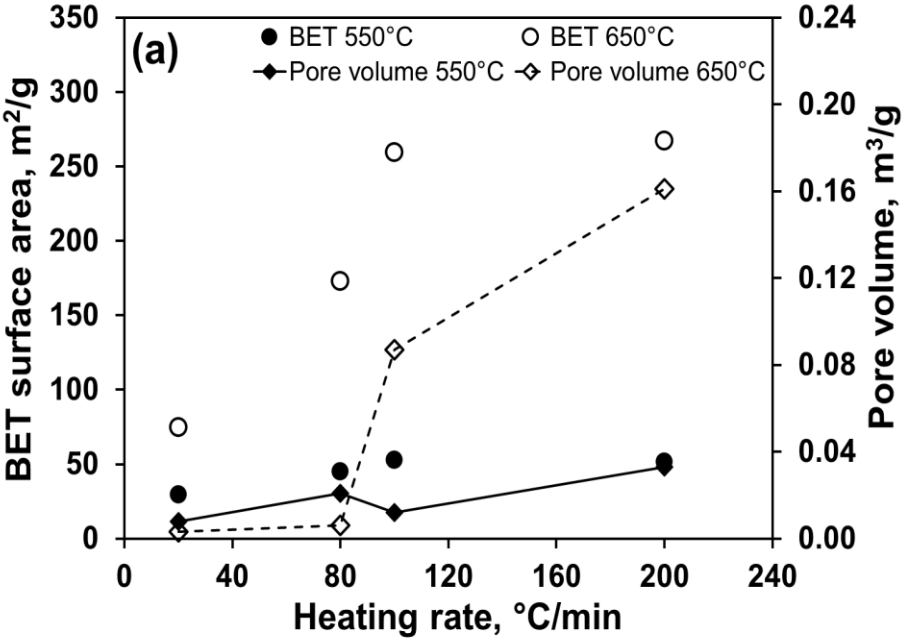


Figure 4-5 Effect of heating rate on the elemental composition of (a) EP char, (b) PF char generated at 550 and 650 °C.

4.4.3. BET surface area and pore size

The specific surface area of the pyrolytic chars, derived from the neat epoxy matrix and phenolic resin under different pyrolysis conditions, were measured by N_2 absorption using BET isotherm. As the range of pore diameter of EP chars and PF chars are from 2.97 nm to 3.44 nm, these pores are classified as mesopore according to the IUPAC nomenclature (Naderi, 2015). For the EP chars, it was found that the pore diameter does not depend on the heating rate, but only on the temperature, i.e. at 650 °C, the average diameter was 3.33 ± 0.10 nm but reduced to 3.15 ± 0.07 nm when the pyrolysis temperature was lowered to 550 °C. On the contrary, for the PF chars, the pore diameter depended on neither heating rate nor pyrolysis temperature because the measured average diameter was 3.13 ± 0.15 nm and 3.19 ± 0.09 nm at 550 °C and 650 °C respectively.

Figure 4-6 (a) shows the effect of heating rate on BET surface area and pore volume of the EP char. A sharp rise in surface area at the early stages of increasing heating rate can be observed from the tests undertaken at 650 °C pyrolysis temperature and the effect later reached a plateau toward 200 °C/min and attained a maximum surface area of 267.2 m^2/g. Similar trend was also noticed from the 550 °C tests, despite a gentler rise at the beginning and the highest surface area at 200 °C/min was only 51.6 m^2/g. It was also apparent that higher heating rate was effective in increasing the pore volume and again a stronger effect was demonstrated from the higher pyrolysis temperature. The pyrolytic effects on BET surface area and pore volume of PF chars are shown in Figure 4-6 (b). A linear correlation between BET surface area and heating rate can be observed from the tests undertaken at both pyrolysis temperatures, for example, at 550 °C, the BET surface area gradually increased from 33.58 m^2/g at heating rate of 20 °C/min to 56.23 m^2/g at 200 °C/min and the value could be further increased by 175 % to 155.09 m^2/g by bringing up the pyrolysis temperature to 650 °C. Again, an explicit and direct influence of the two pyrolytic conditions on PF chars' pore volume can be seen, which also revealed a sudden rise in the pore volume when the heating rate was increased from 80 to 100 °C/min. Numerous investigations had reported that rapidly heated coals created chars with greater surface area, due to fast escaping rate of volatiles which promoted formation of high porosity level (Cai et al., 1996; Radović et al., 1983). Similar effect of pyrolysis temperature on char surface area has also been widely reported, particularly in carbonisation process for making activated carbon structure in an inert environment. Daud et al. (2000) reported that a greater amount of volatiles would be released if a higher temperature was used for the carbonisation process, which increased pore surface area of the resultant activated carbon. An investigation by Li et al. (2008) also concluded that the release of extra volatiles increased BET surface area, total volume and microporous volume char. Higher porous structures in char favour oxygen diffusion, which leads to a higher combustion reactivity in the oxidation process (Wu et al., 2013). This is in agreement with both of the EP and PF chars produced in this study, as the chars with the lowest PT and BT temperatures had the highest BET surface area.



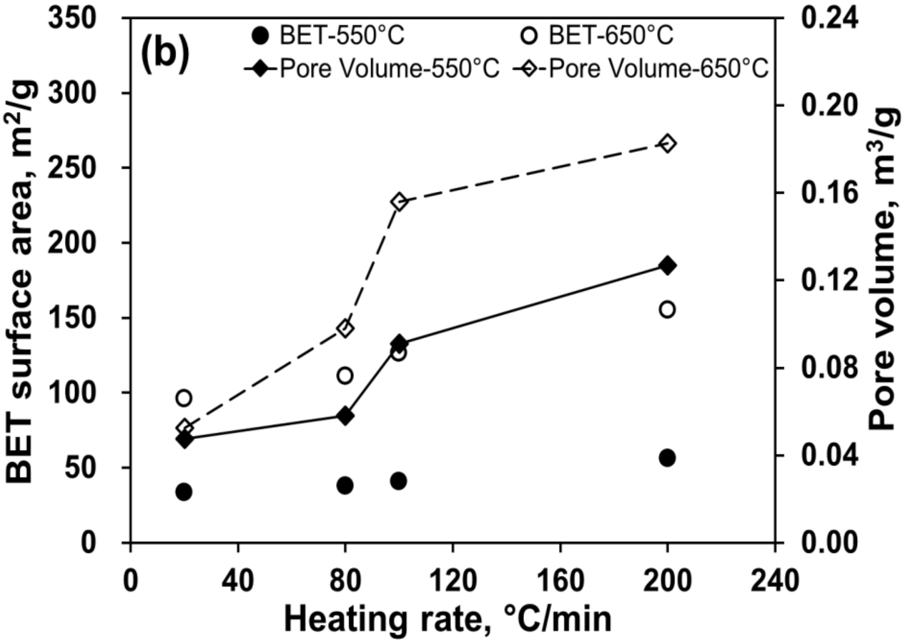
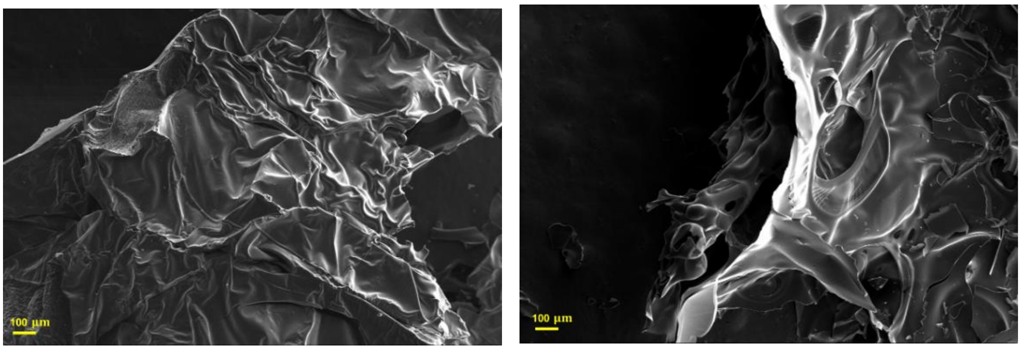


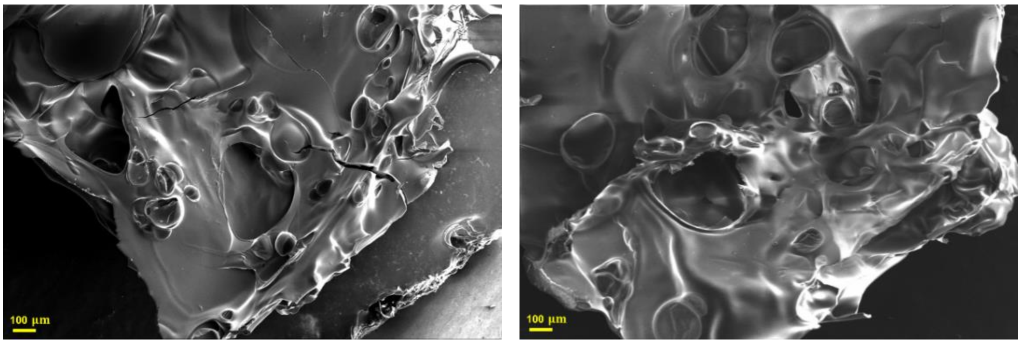
Figure 4-6 Effect of heating rate on BET surface area and pore volume of (a) EP char and (b) PF char generated at 550 °C and 650 °C.

4.4.4. Scanning Electron Microscopy (SEM)

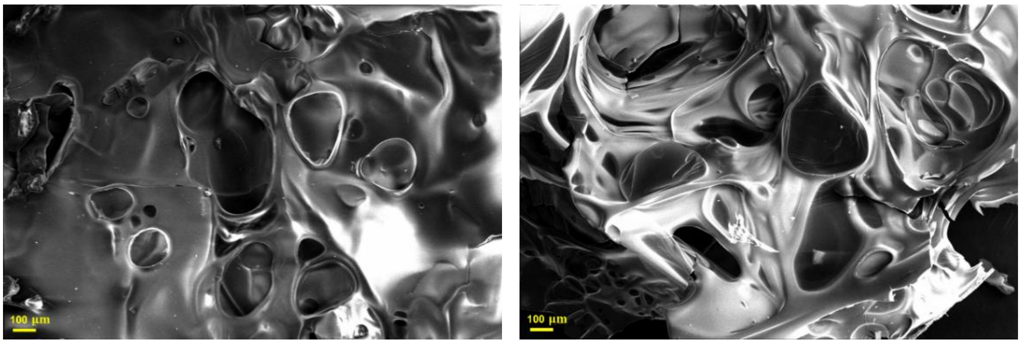
The surface morphology of pyrolytic chars derived from the neat epoxy and phenolic resins were studied via SEM images and the results are shown in Figure 4-7 and Figure 4-8 respectively. Figure 4-7 clearly shows that EP char with a continuous morphology was created under the lowest heating rate and temperature. This is in line with the lowest BET surface area reported in Figure 4-6 (a). Porosity and disintegration became more apparent with higher heating rate and their intensities were increased further with higher pyrolysis temperature. However, a heating rate higher than 100 °C/min did not favour further porosity development nor pore size enlargement, and this agreed well with the plateau regions shown in Figure 4-6 (a) for the EP char. The PF chars, as shown in Figure 4-8, can be seen to have a rather smooth appearance at the lowest heating rate at 550 °C, but their morphological transformation still shares the same trend as the EP chars, namely porous structure and roughness increasing with heating rates and pyrolysis temperature. In general, the PF chars showed a smoother surface compared to the EP chars at any given pyrolytic condition. This was consistent with the lower BET surface area and pore volume measured for the PF chars. An increase in porous structure was found from coal char produced using a rapid heating rate in a pyrolysis process reported by Liu et al. (2020) and this was attributed to a sharp release of volatile components at a higher heating rate, with an overpressure merging smaller pores to produce large cavities and a more open structure in char (Guerrero et al., 2005). It was also reported that more cracks and pores structure could be observed in the chars with higher pyrolysis temperature (Zeng et al., 2015a). Presence of high porous structure promotes diffusion of gas species, such as oxygen penetration and escape of volatiles (Septien et al., 2018) and this likely contributed to the increase in intrinsic reaction found from this study.



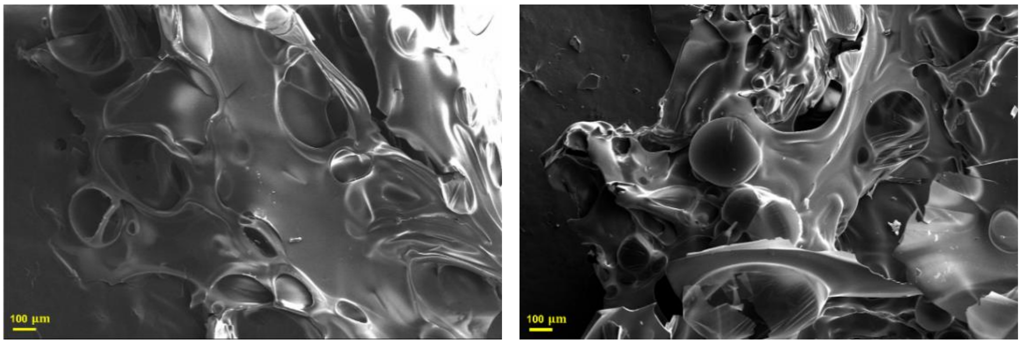
(a) 550 °C-20 °C/min (e) 650 °C-20 °C/min



(b) 550 °C-80 °C/min (f) 650 °C-80 °C/min

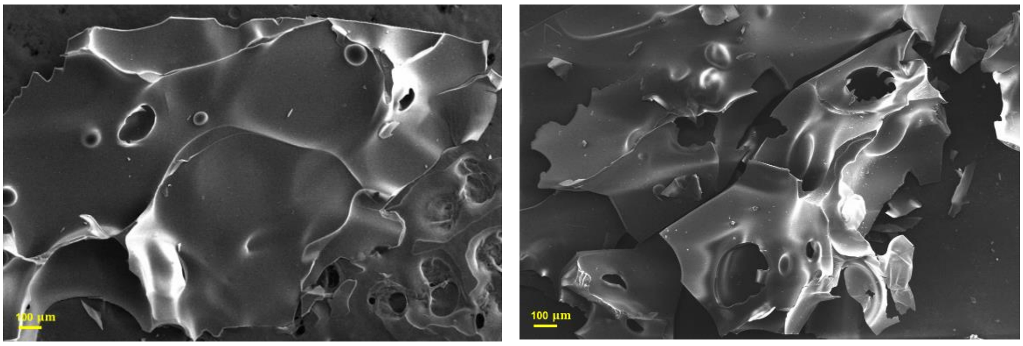


(c) 550 °C-100 °C/min (g) 650 °C-100 °C/min

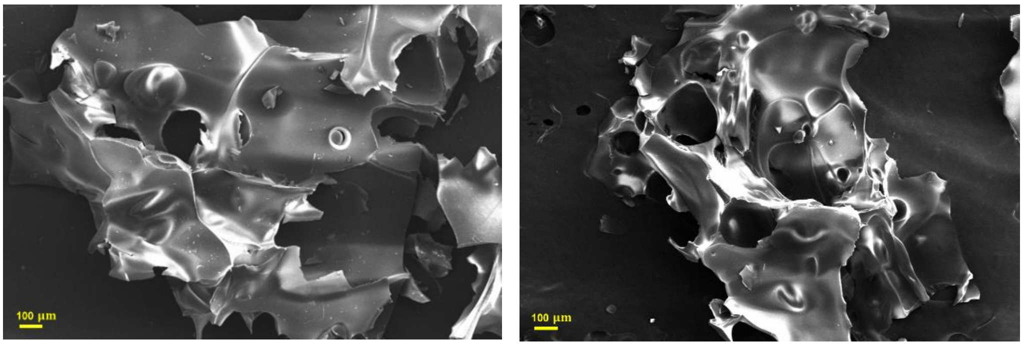


(d) 550 °C-200 °C/min (h) 650 °C-200 °C/min

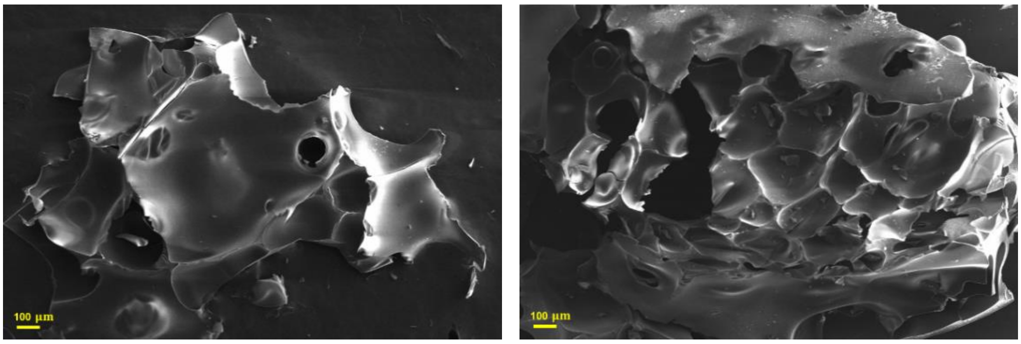
Figure 4-7 SEM images of epoxy resin pyrolytic char showing the effects of heating rates and two pyrolysis temperature, i.e. 550 °C (a, b, c, d) and 650 °C (e, f, g, h).



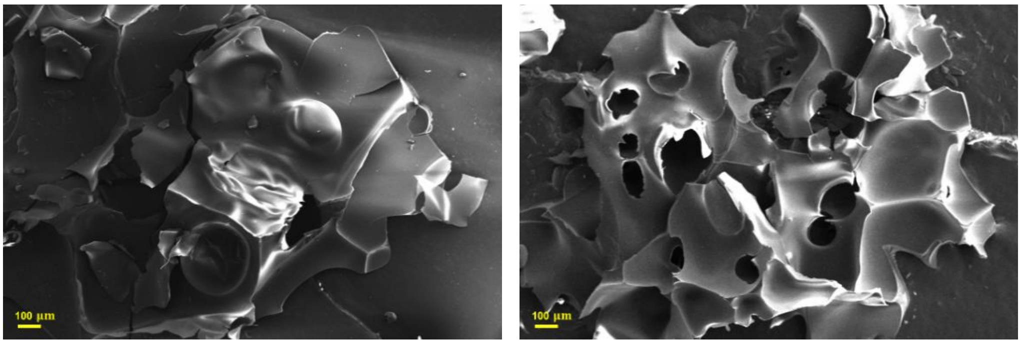
(a) 550 °C-20 °C/min (e) 650 °C-20 °C/min



(b) 550 °C-80 °C/min (f) 650 °C-80 °C/min



(c) 550 °C-100 °C/min (g) 650 °C-100 °C/min



(d) 550 °C-200 °C/min (h) 650 °C-200 °C/min

Figure 4-8 SEM images of phenolic resin pyrolytic char showing the effects of heating rates and two pyrolysis temperature, i.e. 550 °C (a, b, c, d) and 650 °C (e, f, g, h).

4.5. Conclusion

In this chapter, different pyrolytic conditions were applied to carbon fibre epoxy prepreg and carbon fibre phenolic prepreg in TGA. The comparisons in char retention, pyrolytic char intrinsic reactivities, elemental analysis and specific surface area between prepregs and their derived chars were investigated. The result showed that pyrolytic chars derived from both the CF/EP prepreg and CF/PF prepreg could also be reduced by optimising the pyrolytic reaction conditions, particularly the increasing heating rate and raising pyrolysis temperature. The least char formation was obtained at the highest temperature of 650 °C with a fastest heating rate of 200 °C/min in this research. However, the extend of char reduction of CF/PF prepreg was less significant compared to char from CF/EP prepreg, probably due to a high molecular weight aromatic structure associated with the phenolic resin. A further study on intrinsic reactivity of the chars derived from neat resins was performed to investigate their degradation behaviour in an oxidising environment. High heating rate and temperature produced chars with lower peak and burnout temperatures, indicating an increase in the intrinsic reactivity and this applied for both EP and PF chars. Nevertheless, the PF chars had a lower intrinsic reactivity and this was as expected as phenolic resin is generally used as an ablative material for its high resistance to flammability. The improvement in intrinsic reactivity had been attributed to the rise in oxygen-to-carbon ratio, pore size and BET surface area. The display of high porous structure on the char surface, as shown in the SEM images, further consolidated the effect of pyrolytic conditions on the char intrinsic reactivity. It can be concluded that appropriate selection of pyrolytic reaction conditions, not only reduce the char yield but also improve the char oxidation kinetic.

Chapter 5. Hybrid recycling method

5.1. Introduction

In this chapter, a new hybrid method of chemical pre-treatment process followed by a conventional pyrolysis is proposed. This method aims to reduce char formation in the pyrolysis stage. Ultimately, clean carbon fibre could potentially be recycled in a shorter oxidation duration, which not only reduces energy consumption, but preserves better mechanical performance of the recycled fibre due to the reduced oxidative damage at high temperature. The combined process of chemical pre-treatment and pyrolysis is shown in Figure 5-1. The carbon fibre reinforced epoxy (CF/EP) prepreg was immersed in the 40 wt.% zinc chloride/ethanol pre-treatment agent at 80 °C for two hours. Then, after the washing and drying, the treated prepreg was pyrolyzed in a sliding tube furnace at 650 °C for 30 minutes.

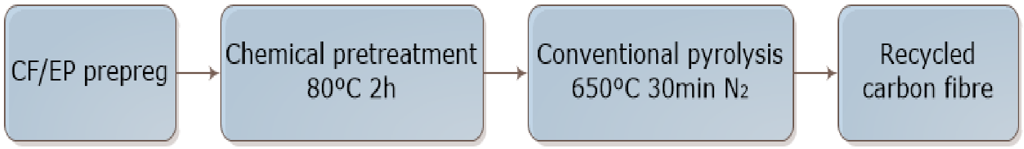


Figure 5-1 Process of hybrid recycling method.

As a comparison, the as-received CF/EP prepreg was pyrolyzed and then oxidized using the standard conventional pyrolysis recycling method in the tube furnace. The process is shown in Figure 5-2.

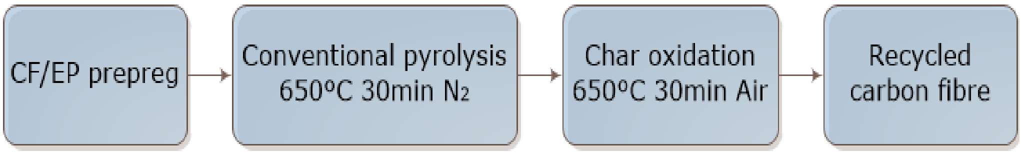


Figure 5-2 Process of standard conventional pyrolysis.

Characterizations focused on pre-treated CF/EP prepreg and recycled carbon fibre collected from both a hybrid recycling method and standard conventional pyrolysis to evaluate the effect of pre-treatment on the degradation behaviour of prepreg and the quality of fibre via TGA (see Section 5.2), fibre tensile tester (see Section 5.2.4), Raman spectroscopy (see Section 5.2.6), XPS (see Section 5.2.7), and SEM (see Section 5.2.7). The test sample code is listed in Table 5-1 .

Table 5-1 Sample code and description.

Sample code	Description
vCF	Virgin carbon fibre
rCF	Recycled carbon fibre
rCF-pretreated	Fibre recycled from hybrid recycling method
rCF-oxidized	Fibre recycled from standard conventional pyrolysis

5.2. Results and discussions

5.2.1. Thermal behaviour of prepregs

The conventional pyrolysis behaviours of the as-received prepreg and pre-treated prepreg in nitrogen atmosphere were investigated; their mass loss profile over the temperature range is shown in Figure 5-3. For the as-received prepreg sample, after a negligible drop at the early stage of the heating process, from around 420 °C, the profile undergoes a sharp drop in mass and then reaches a relatively flat plateau; the mass continues to drop when the temperature is maintained at 650 °C. The initial negligible drop was mainly due to moisture loss, whilst conversion of epoxy matrix into volatiles is attributed to the sharp loss in mass. The same pattern was observed from the pre-treated sample, but the start temperature of sharp mass loss was around 390 °C. In addition, the mass loss of pre-treated prepreg was lower than the as-received prepreg due to the removal of some resin in the early pre-treatment process. DTG curves of the corresponding samples are shown in Figure 5-4; both show only one peak, which can be attributed to the epoxy resin devolatisation, a fundamental mechanism of the pyrolysis process (Biagini et al., 2006) in recovery of carbon fibre. It can be seen that the peak of the pre-treated sample was further to the left, indicating that the devolatilisation stage commenced and finished at lower temperatures (Shamsuddin and Williams, 1992). The devolatilisation temperature of the pre-treated composite reduced by around 30-40 °C and the peak temperature was 40-50 °C lower. Therefore, the chemical pre-treatment process was proved to be effective in reducing the pyrolysis temperature.

In addition, at the end of the TGA test, it was found that the as-received prepreg samples remained intact and stiff, as shown in Figure 5-5 (a), indicating a significant presence of pyrolytic char residues on the fibre surface. However, it is evident that loose fibres were recovered from the pre-treated samples, as shown Figure 5-5 (b). Such reductions in pyrolysis temperature and char formation from the pre-treated samples are attributed to the combined effects of the $ZnCl_2$/ethanol pre-treatment agent; ethanol has a high swelling ability which opens up the epoxy structure in the prepreg to facilitate penetration of the $ZnCl_2$ to cause cleaving of C-N bonds in the epoxy's cross-linked 3D structures (Deng et al., 2015; Liu et al., 2017).

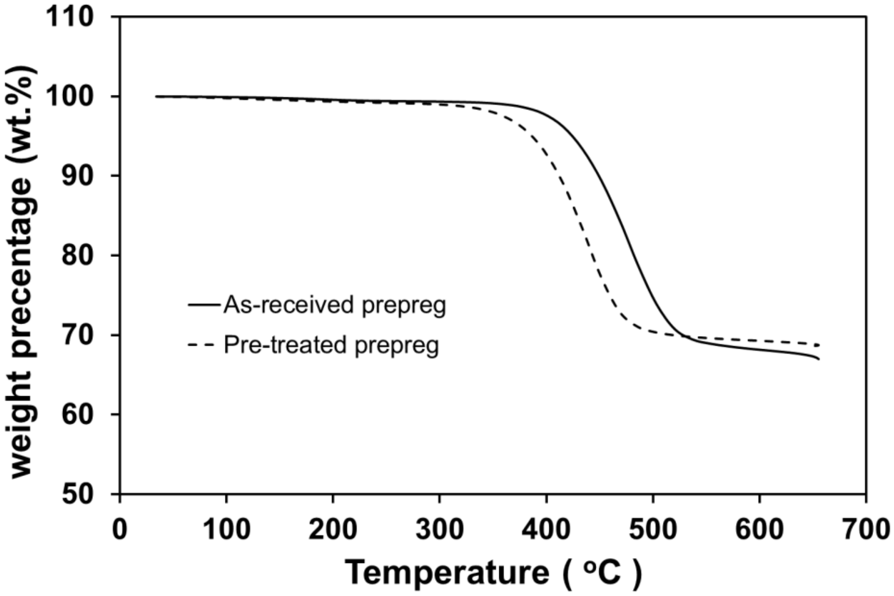


Figure 5-3 The mass change with temperature (TG curve) of the as-received and pre-treated prepregs.

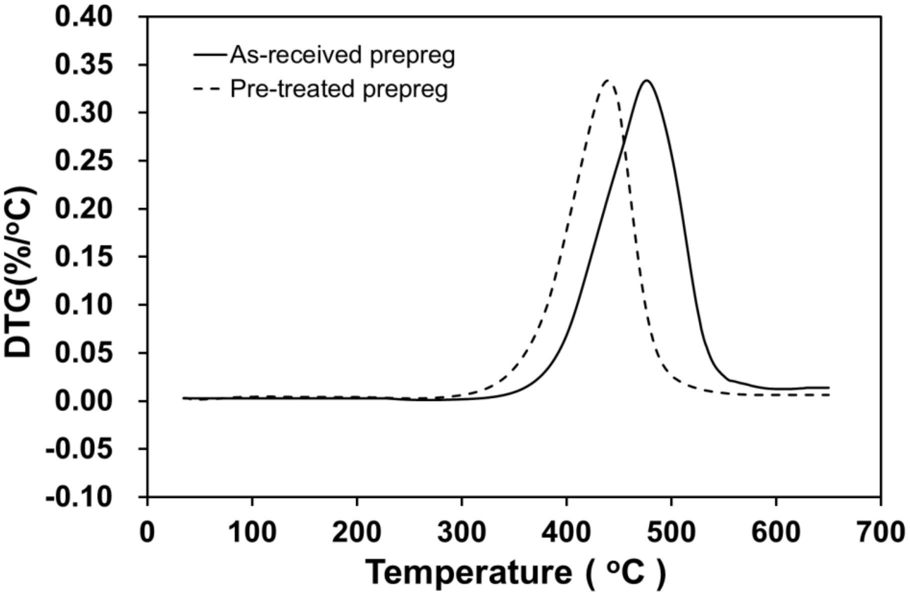


Figure 5-4 The derivative of mass change with temperature (DTG curve) of the as-received and pre-treated prepregs.

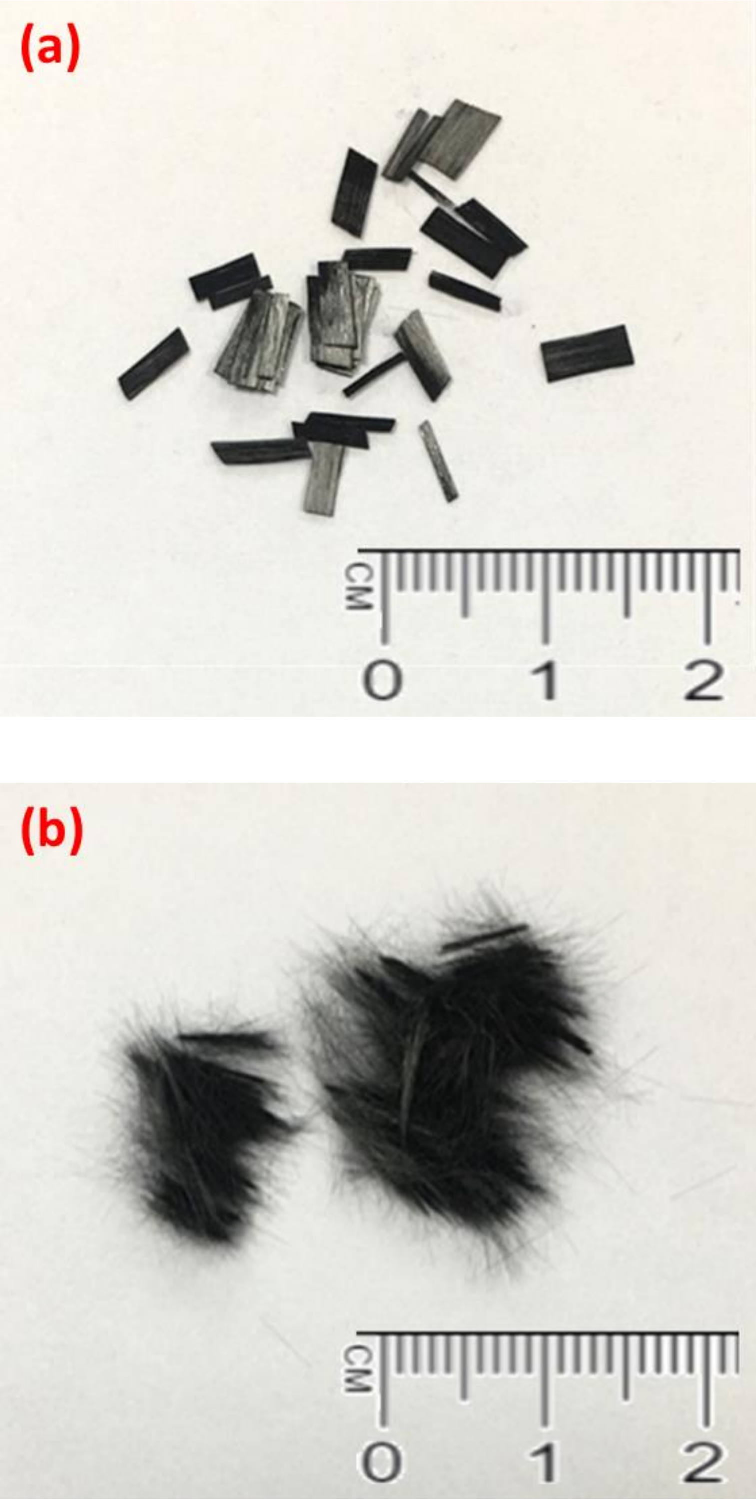


Figure 5-5 Pyrolysis solid product from (a) as-received prepregs and (b) pre-treated prepregs

5.2.2. Surface morphology of the pre-treated prepreg

The effect of chemical pre-treatment on prepreg surface morphology is depicted in SEM pictures shown in Figure 5-6. It can be seen that without the pre-treatment, the morphology of the as-received prepreg (Figure 5-6 (a)) shows that the fibres were fully covered by the epoxy resin and exhibited a smooth morphology. On the contrary, as shown in Figure 5-6 (b), after the chemical pre-treatment, the prepreg exhibited a rough morphology together with the presence of cracks and tiny voids in the epoxy matrix. The change in surface morphology indicates the effectiveness of the pre-treatment process to initiate a breakdown of the cross-linked structure of the epoxy matrix. The swelling ability of ethanol and the coordinate ability of Zn^{2+} with N atoms potentially degrades the epoxy (Deng et al., 2015).

In addition, a lab-made carbon fibre reinforced epoxy (CF/EP) plate was pre-treated under the sample condition as prepreg and its macro surface morphology was observed through an optical microscope. Figure 5-7 shows the surface of CF/EP composite plate before and after the chemical pre-treatment. Figure 5-7 (a) shows that the surface of the original CF/EP composite plate is relatively smooth and the defects on the surface have relatively smooth edges. After chemical pre-treatment, the CF/EP composite plate shows a relatively rough surface with stripes, which could be the texture of fibre tows. Meanwhile, the defects appeared with incomplete edges. These figures help to prove the degradation of epoxy in the $ZnCl_2$/ethanol catalytic system.

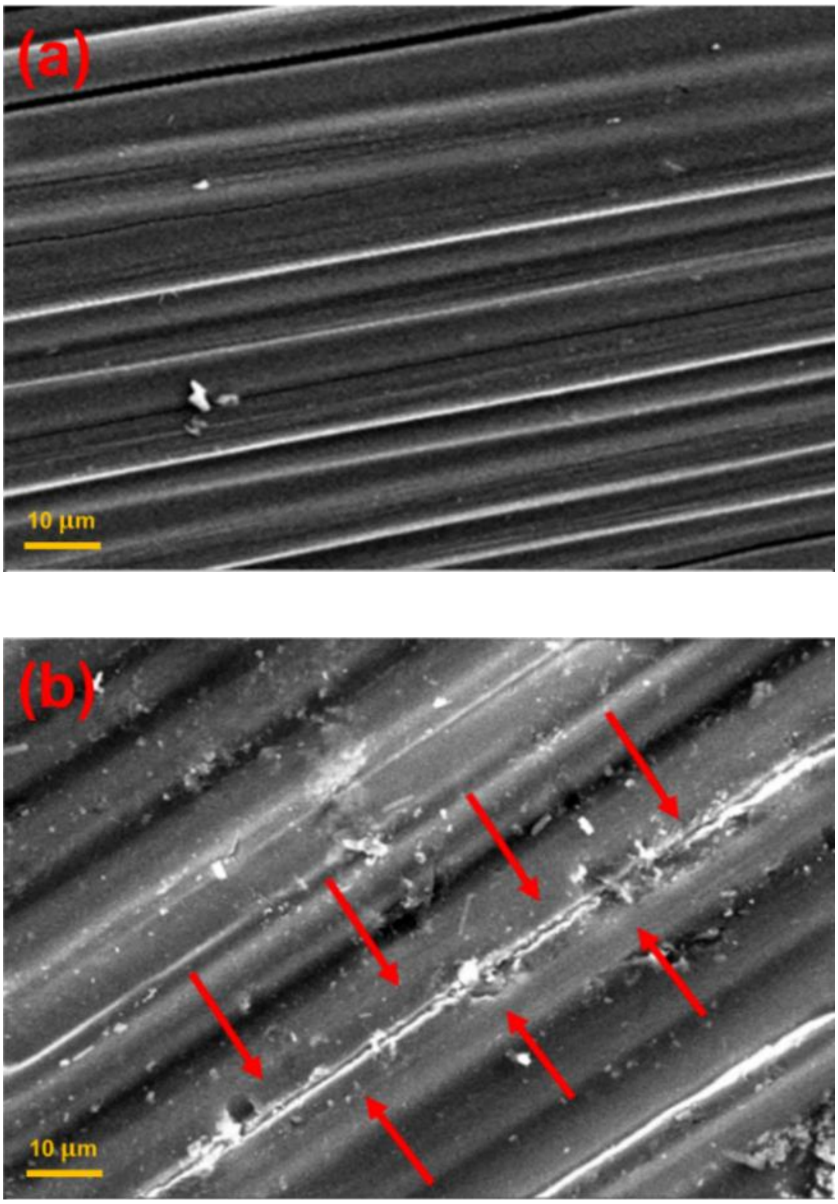


Figure 5-6 The SEM image of (a) the as-received CF/EP prepreg and (b) the pre-treated CF/EP prepreg.

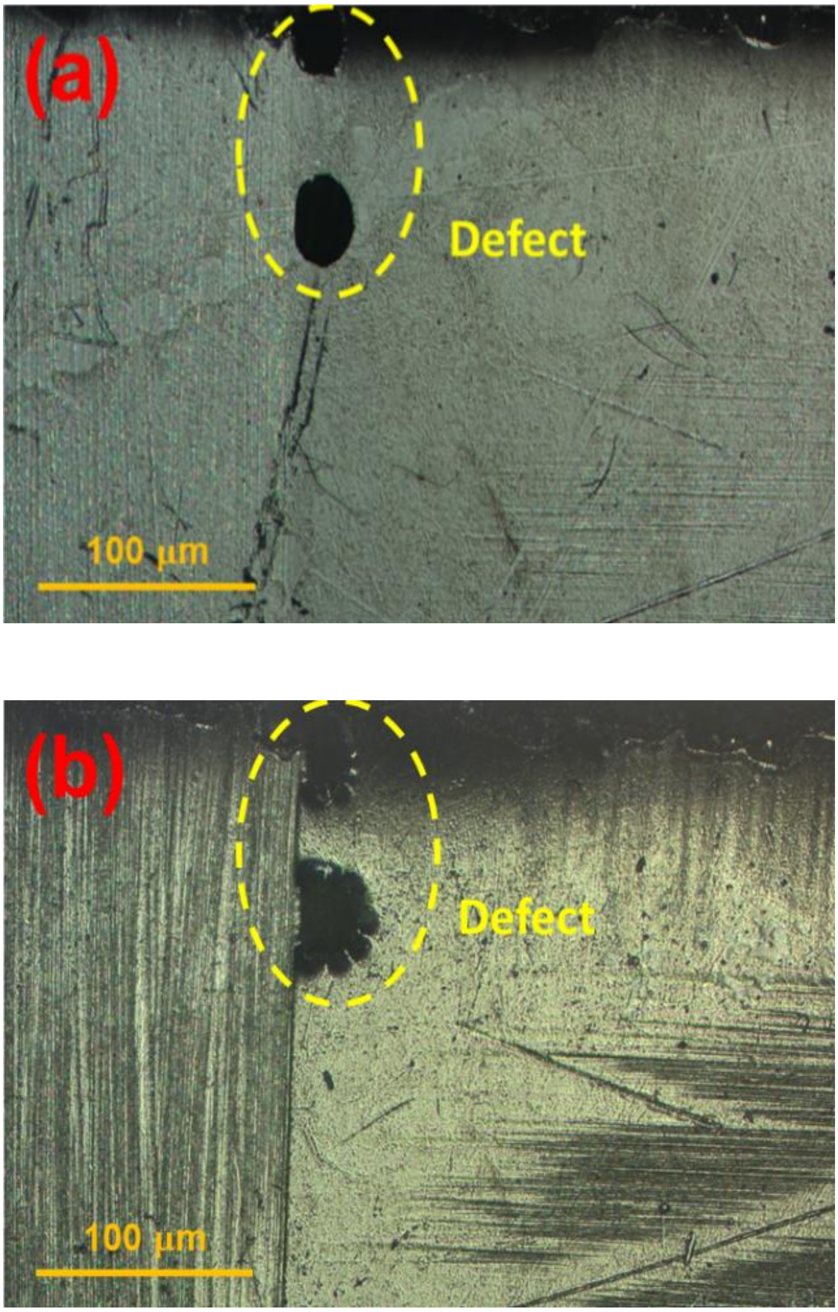


Figure 5-7 The surface of CF/EP composite (a) before and (b) after the pre-treatment.

5.2.3. Elemental analysis of prepreg

The elemental analysis of prepreg before and after the chemical pre-treatment was determined by SEM/EDS test to analyse the residue of Zn and Cl element and the results are shown in Table 5-2. The carbon and oxygen element were detected for the as-received prepreg with the relative content of 84.68 wt.% and 15.32 wt.% respectively. After the pre-treatment process, the Zn and Cl element appeared on the surface of prepreg and the relative content of them was 4.88 wt.% and 3.01 wt.% respectively after the cleaning and drying process. There was not a significant residue of Zn and Cl on the surface of the pre-treated prepreg before the pyrolysis process.

Table 5-2 The surface element of the as-received prepreg and the pre-treated prepreg.

Element (wt.%)	As-received prepreg	Pre-treated prepreg
C	84.68	77.69
O	15.32	14.42
Cl	-	4.88
Zn	-	3.01

5.2.4. Single fibre tensile test of carbon fibre

Tensile properties of the recovered carbon fibres were characterized by using a single fibre tester. The results are presented in Table 5-3, which also includes data measured from the virgin carbon fibres. There was 0.9 % and 5.3 % reduction in tensile modulus for rCF-pretreated and rCF-oxidized, respectively, compared to that of vCF. The average diameter and Weibull tensile strength of vCF is 6.82 micron and 4670 MPa. The rCF-pretreated and rCF-oxidized showed reductions of 4 % and 10 % in diameter, respectively. The Weibull tensile strength of rCF-pretreated and rCF-oxidized decreased by about 8.20 % and 16.06 %, respectively. Extra char oxidation is probably the main reason for the strength reduction of rCF-oxidized because carbon fibres also undergo the same oxidation process, thus its mechanical performance is greatly affected. Degradation in diameter and tensile strength have been observed from fibre recovered from a previous conventional pyrolysis process (Yang et al.). Due to the prolonged oxidation process for char removal at high temperature, 28 % reduction in tensile strength has been reported by Lopez et al. (2013). Pimenta & Pinho (2012) also reported the importance of controlling the pyrolysis condition to avoid a significant drop in fibre diameter and tensile strength. Up to 21% and 85% reduction in diameter and tensile strength of rCF was reported if an aggressive oxidation condition was used (Pimenta and Pinho, 2012). In this work, rCF-pretreated retained 91.8% of tensile strength of the vCF and required no further oxidation process, confirming the benefit of the pre-treatment process.

Table 5-3 The tensile properties virgin carbon fibre and recycled carbon fibre.

Sample	Diameter (micron)	Tensile modulus (GPa)	Tensile strength (MPa)	Retention rate (%)
vCF	6.82±0.15	210.03±19.43	4670	100
rCF-pretreated	6.60±0.24	208.15±17.29	4287	91.80
rCF-oxidized	6.19±0.26	198.85±21.64	3430	73.44

5.2.5. Surface element analysis of carbon fibre

XPS analysis was used to detect changes in the surface functional groups of the carbon fibres. The XPS wide spectrum of the virgin fibre, rCF-oxidized and rCF-pretreated are shown in Figure 5-8. From the XPS wide spectrum, three peaks assigned to C 1s (285 eV), O 1s (531 eV) and N 1s (402 eV) were detected for both vCF and rCF, representing the main components of the carbon fibres. The surface element composition was analysed and is listed in Table 5-4. The rCF-pretreated showed a similar composition in C and O elements as that of rCF-oxidized, but a decrease in N element was observed. Also, a negligible composition of Zinc and Chlorine element, around 1 to 1.5 %, was detected; this comes from the pre-treatment system. The vaporization temperature of $ZnCl_2$ is around 400 °C (Jones et al., 2013), which is much lower than the 650 °C pyrolytic temperature undertaken in this study. The negligible composition of Zn and Cl elements on the surface of rCF-pretreated suggests that no further cleaning process is required. Compared with the vCF, the increase in nitrogen of the rCF could be the residue of the PAN precursor in the carbonization process (Cazeneuve et al.), this is because the sizing has been removed through the recycling. The Nitrogen on the rCF-pretreated is lower than that of rCF with oxidization, this decrease can possibly be attributed to the cleavage of C-N bond by $ZnCl_2$ (Wang et al., 2015a). The atomic O/C ratio is a quantitative measurement of oxygen-containing functional groups on carbon fibre surfaces and a good indicator of the effective surface area of chemical bonding between carbon fibres and resins (Yip et al., 2002). The O and O/C ratio of both rCF were lower than the vCF sized by epoxy, this indicates lower surface activity than vCF (Yue et al., 1999).

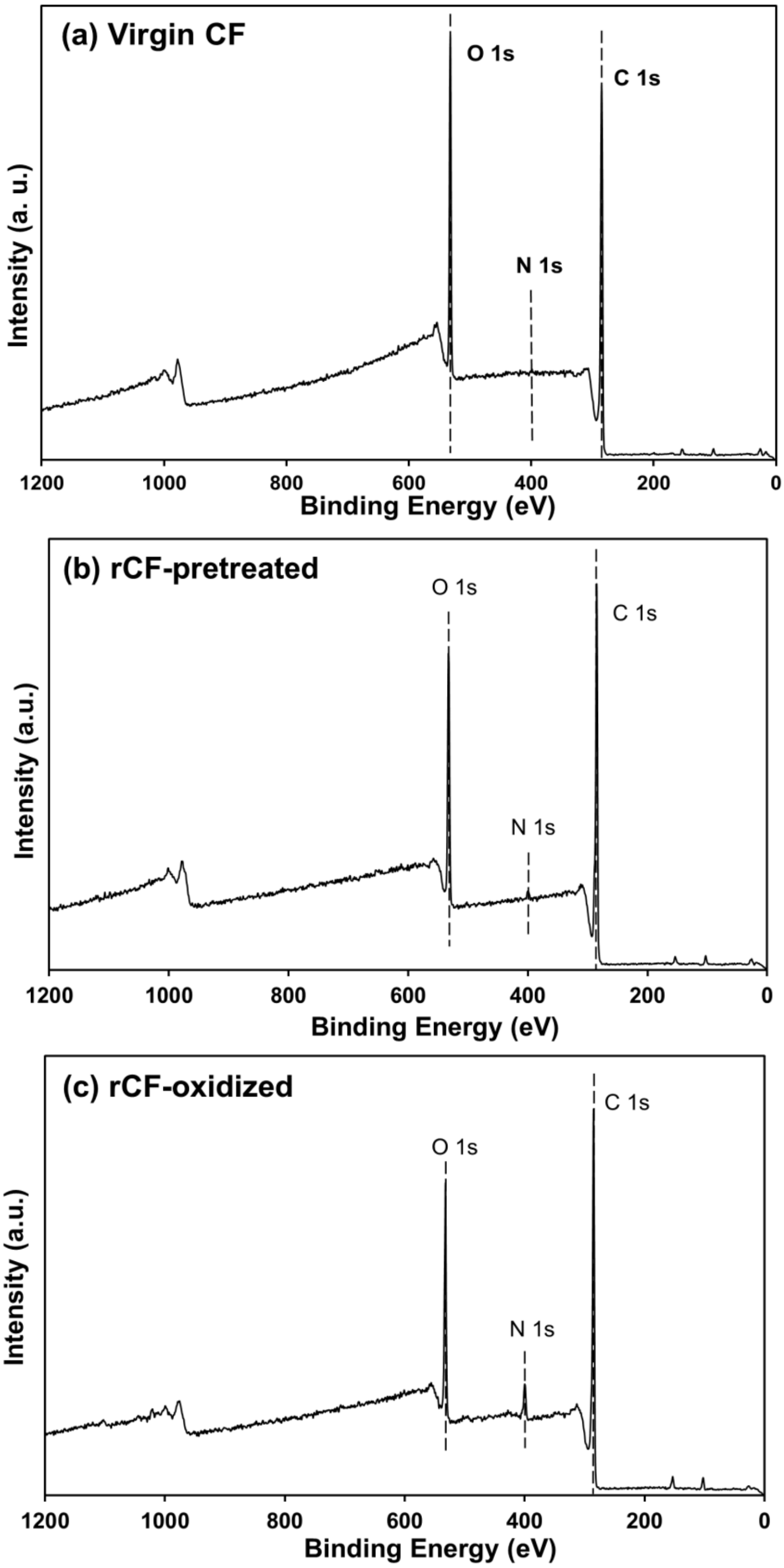


Figure 5-8 XPS wide spectrum of (a) vCF, (b) rCF-pretreated and (c) rCF-oxidized.

Table 5-4 Elemental composite for recycled carbon fibre.

Samples	Element composition (%)					
	C 1s	O 1s	N 1s	Zn 2p	Cl 2p	O1s/C1s
vCF	77.10	22.39	0.51	-	-	0.29
rCF-pretreated	79.76	14.05	3.47	1.36	1.19	0.18
rCF-oxidized	79.44	15.00	5.56	-	-	0.19

The functional groups on the fibre surface were clarified in C 1s high resolution narrow spectrum. The C 1s narrow spectrum was curve-fitted to component peaks of C–C (284.4 eV) (Terzyk, 2001), C-O- or C-OH (285.4-286.3) (Terzyk, 2001), and C=O or COO- (287.2-289.3) (Terzyk, 2001) according to the binding energy. The fittings are shown in Figure 5-9 and the relative content of the functional group is listed in Table 5-5. The surface functional groups of rCFs are similar to that of the vCF but in variable atomic concentration. The C-C bond is the main functional group of both vCF and rCF. The vCF has the highest content of C-O- and of the C-OH group, probably due to the epoxy sizing. The content of the C-C bond of rCF-pretreated was much higher than that of vCF and rCF-oxidized, which is similar to the virgin fibre after sizing removal (Jiang et al., 2008) in a previous study. Previous research reports that the C-O- or C-OH group can be removed in pyrolysis at high temperature (Zielke et al., 1996), so the oxygen containing group on the surface of rCF indicates the reaction between carbon fibre with oxygen and the exposure of the fibre without sizing. The concentration of C-O- or C-OH group of rCF-oxidized was higher than that of rCF-pretreated due to the extra oxidation and may cause the decrease of mechanical properties of rCF-oxidized (Yang et al., 2015). The C-O- groups were also detected in the surface of rCF-pretreated, these may come from the residue of resin, which was observed in the SEM picture of the rCF-pretreated. Jiang et al. (2009) studied the surface chemistry of rCF and reported that the C-O- group may be transformed to the C=O- and O-C=O group when the carbon fibre begins to oxidise. The content of C=O or COO- of rCF-oxidized is higher than both that of vCF and rCF-pretreated, this may be caused by the fibre oxidation. The increase in oxygen containing groups (C-O-,C=O-) of rCFs indicates the occurrence of a chemical reaction between carbon fibres and oxygen (Song et al., 2017). Wu et al. (2019) successfully reclaimed carbon fibre from pyrolysis in both molten $ZnCl_2$ and air. They reported that carbon fibre surfaces were protected by molten $ZnCl_2$, which prevented surface oxidation, and the increase in the concentration of C=O- and C–OH of carbon fibre reclaimed in air is due to the mild oxidation. The rCF-oxidized in this work showed similar chemical bonding

(C-C, C-O-, C=O-) with vCF, and therefore it would also be appropriate for bonding to a polymer matrix in a composite (Pickering, 2006). Yamamoto et al. (1971) claimed that the C=O- group on the fibre potentially helps the fibre-wetting property. Moreover, the rCF-pretreated showed a similar surface chemical bonding as the virgin fibre without sizing.

Table 5-5 The relative contents of functional groups on carbon fibre surface.

Sample	C-C 284.6 eV (Terzyk, 2001)	C-O-, C-OH 285.4-286.3 eV (Terzyk, 2001)	C=O, COO- 287.2-289.3 eV (Terzyk, 2001)
Virgin fibre	50.46	42.52	7.02
rCF-pretreated	70.77	16.34	12.88
rCF-oxidized	42.38	40.18	15.44

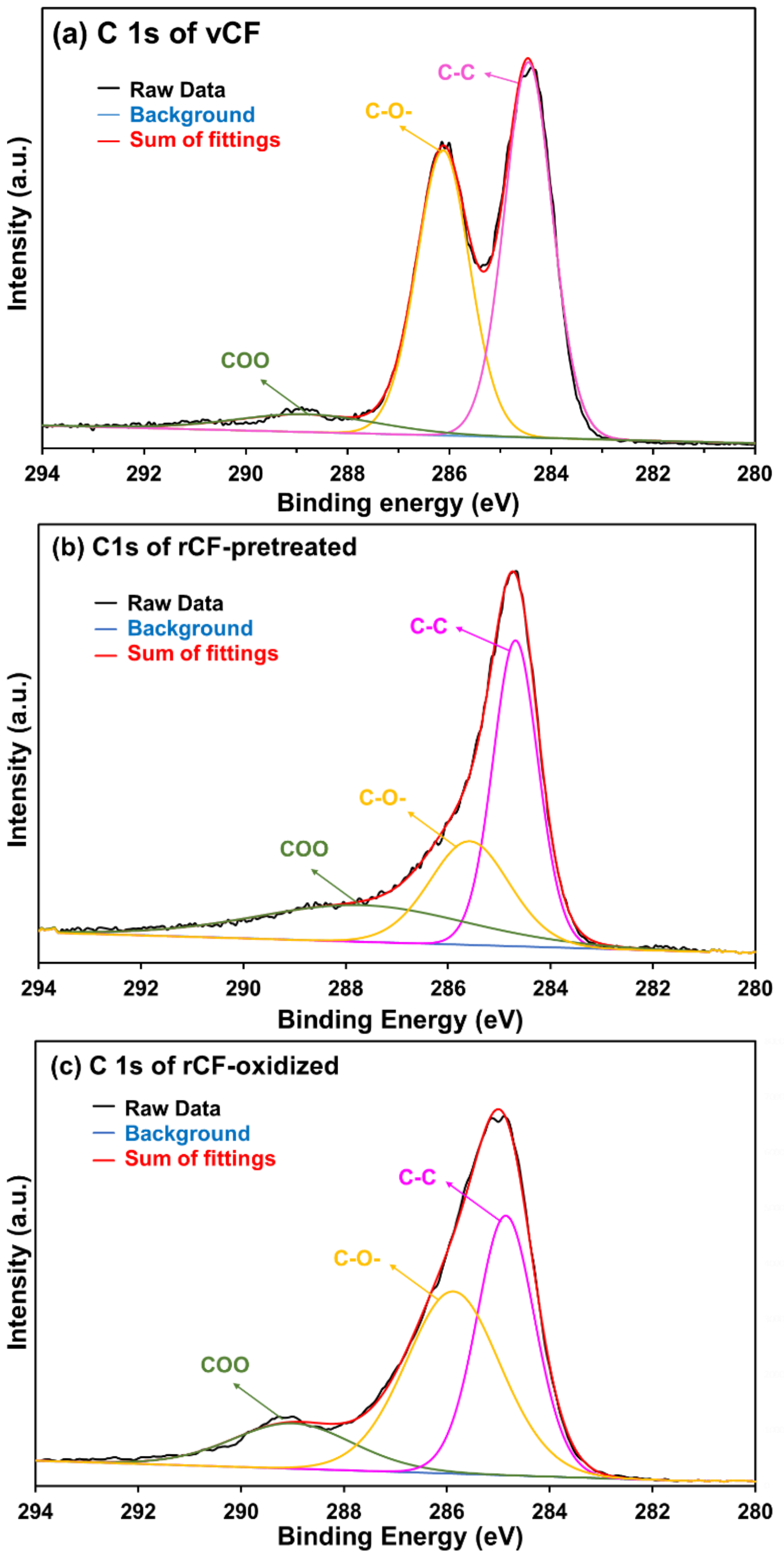


Figure 5-9 C1 high resolution spectrum of (a) vCF, (b) rCF-pretreated and (c)rCF-oxidized.

5.2.6. Raman spectroscopy of carbon fibre

Generally, Raman spectroscopy is a useful approach to analyze amorphous, crystalline, and non-crystalline phases of carbon materials. In this study, Raman spectroscopy was used to investigate the change in graphitization structure of carbon fibres after recycling. For carbon material, there are usually two Raman broad bands at the frequency of around 1350 cm^{-1} and 1580 cm^{-1}, these represent the D (disordered) band and G (graphitic) band, respectively. The D band is assigned to the degree of disorder of the carbon atom structure, and the G band indicates the graphitic lattice structure (Huang and Young, 1995). The degree of disorder ($R=I_D/I_G$) can be quantified by the relative intensity ratio of the D band (I_D) caused by disordered structure and the G band (I_G) caused by graphite crystal. Usually, the smaller R value indicates the lower degree of disorder and higher degree of graphitization of the carbon fibres (Xu et al., 2013). In addition, the full widths at half maximum (FWHM) of the band are a parameter to indicate the degree of graphitic and disordered structure, as the greater the FWHM of the D and G bands, the more disordered the structure (Wu et al., 2019). The Raman spectrum of the virgin and recovered carbon fibres at the range 800 cm^{-1} to 2000 cm^{-1} are shown in Figure 5-10. From these figures, it can be seen that all Raman spectrum exhibit a similar curve and there are two broad Raman bands located at around 1350 cm^{-1} and 1580 cm^{-1}, these represent the D and G bands, respectively.

Table 5-6 Raman spectral parameters of the virgin and recovered carbon fibre.

Sample	**D band**		**G band**		**R**
	Raman shift (cm^{-1})	FWHM	Raman shift (cm^{-1})	FWHM	
vCF	1380.21	291.02	1596.65	106.97	2.94
rCF-pretreated	1380.62	291.83	1595.76	106.52	3.12
rCF-oxidized	1381.48	300.17	1596.79	110.54	3.23

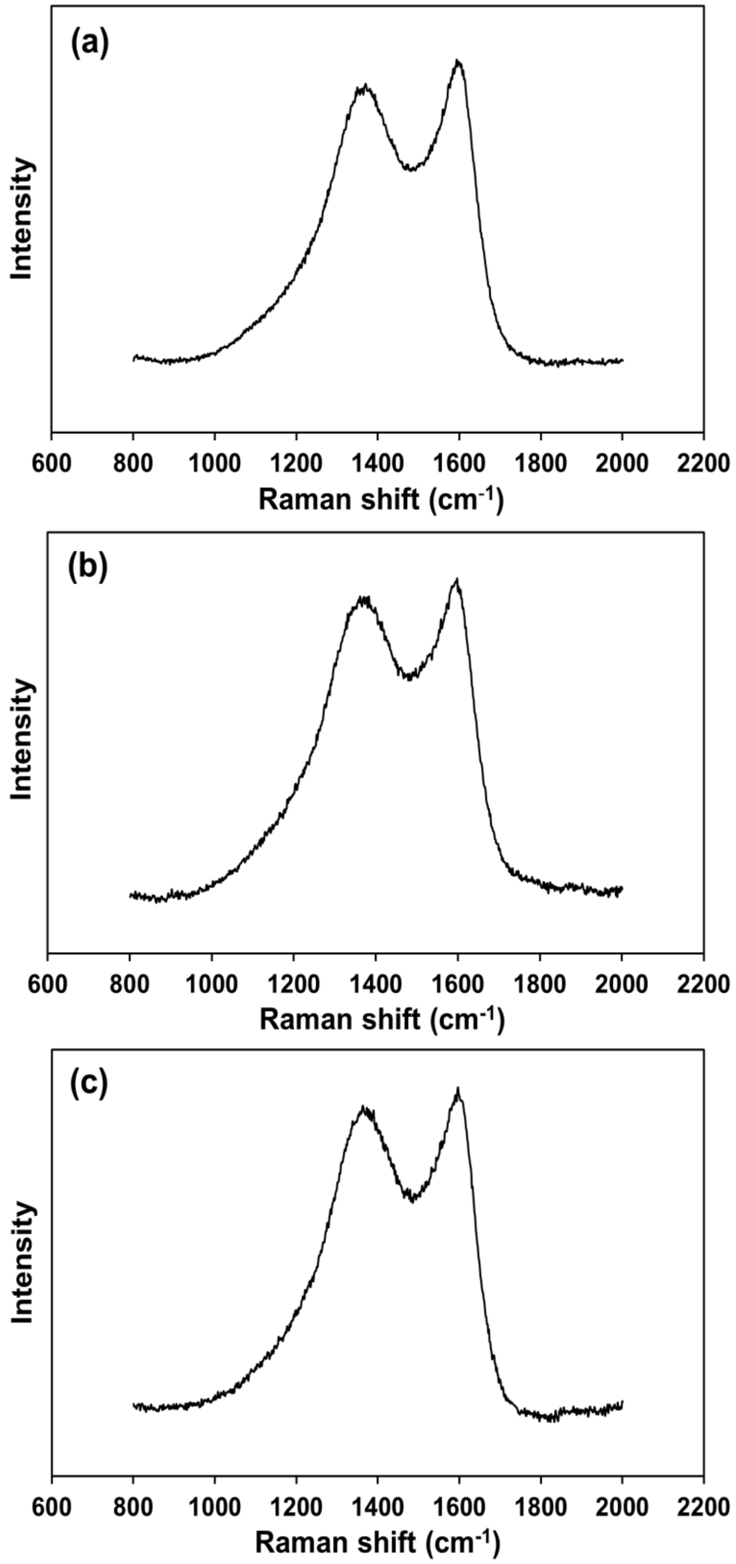


Figure 5-10 The Raman spectra of (a) vCF, (b) rCF-pretreated and (c) rCF-oxidized.

The Gauss peak fitting method was used in the Origin software to determine the Raman parameters; the Raman shift (cm^{-1}), FHWM, and R number are summarised and listed in Table 5-6. It can be seen from the table that the virgin fibre has the smallest R value of 2.94, this indicates that the degree of graphitization of vCF was the highest. Compared to the vCF, the R value of rCF-pretreated and rCF-oxidized increased by 0.18 and 0.29, respectively, indicating that the degree of graphitization of recovered fibre decreased slightly. The rCF-oxidised shows more damage in graphitization structure due to the lower R value in comparison to the fibre rCF-pretreated; this could explain the decrease in fibre tensile modulus. The FWHM values of the D band and the G band of virgin fibre are 291.02 and 106.97, respectively. The FWHM value of rCF-pretreated shows a nearly similar value to that of virgin fibre, reflecting the similar degree of graphitization. The FWHM value of rCF-oxidized is higher than both VCF and rCF-pretreated which forecasts a higher degree of disorder. This finding is consistent with the outcome of a change in R value, where the rCF-oxidized performs a lower degree of graphitization. Similar results were concluded by Wu et al. (2019) using pyrolysis with molten $ZnCl_2$, and by Xu et al. (2013) using the chemical recycling with peroxide hydrogen and N,N-dimethylformamide mixture solution. Both studies reported that the degree of graphitization of the rCFs decreased in comparison to the virgin carbon fibre.

5.2.7. Surface morphology of carbon fibre

Surface morphologies of the rCF were observed via SEM to evaluate the effects of chemical pre-treatment. The comparison was made against vCF and the results are shown in Figure 5-11. From Figure 5-11 (a), it can be seen that vCF show a clean, smooth, and complete surface. However, Figure 5-11 (b) shows that the fibre is covered by a significant amount of char merely after pyrolysis in N_2, without either pre-treatment or an oxidation process. This phenomenon demonstrates the importance of char elimination in the application of reuse. Similar continuous and complete fibres were observed from both rCF-pretreated and rCF-oxidized, as shown in Figure 5-11(c) and (d), except for the presence of some char particles scattered on the surface. More char particles were observed on the rCF-pretreated, while the rCF-oxidized shows a cleaner surface as in the virgin fibre. Ma et al. (2020) observed the pyrolytic char on the surface of recycled carbon fibre pyrolyzed in N_2. After the gasification in air, the recycled fibres showed a complete, relatively clean surface. Wu et al. (2019) reported the $ZnCl_2$ has catalytic effects in resin degradation and good compatibility with the epoxy resin, and this promotes the detachment of resin with fibre. Their SEM images show that fibres recovered in molten $ZnCl_2$ exhibit a very clean surface. In this work, these SEM pictures emphasize the effectiveness of the pre-treatment process in reducing the char residue.

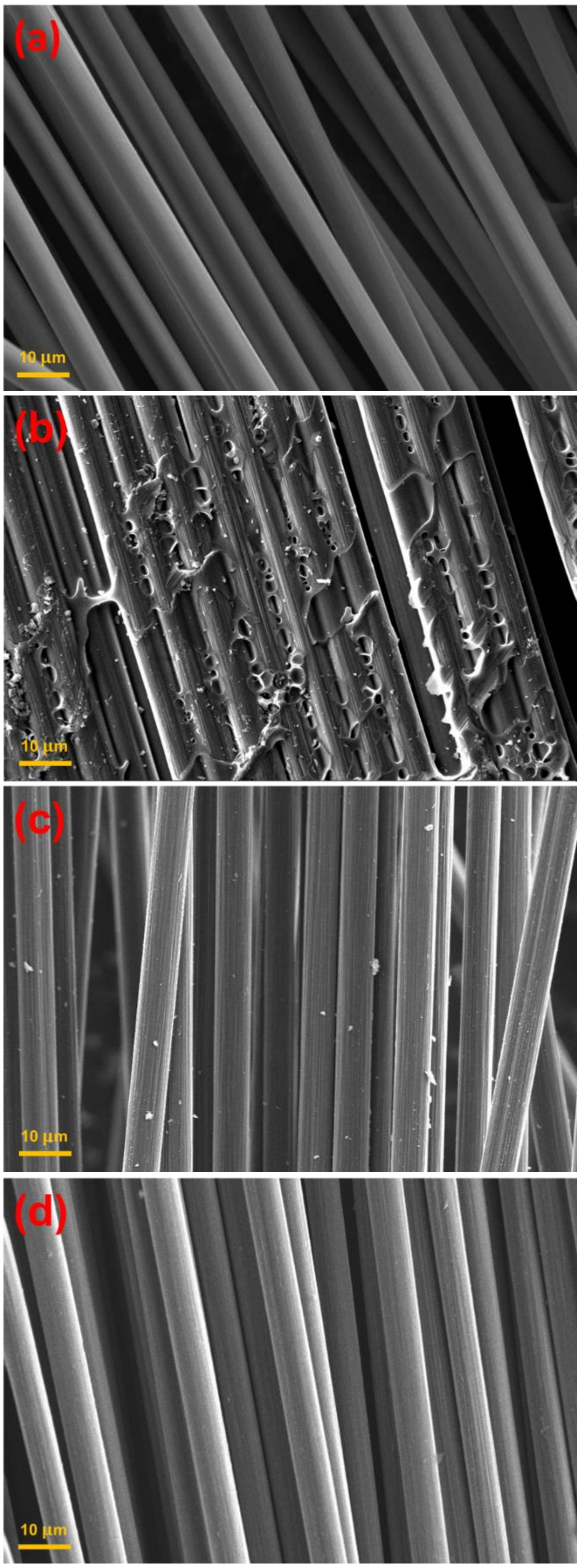


Figure 5-11 The SEM images of (a) virgin carbon fibre, (b) rCF with char, (c) rCF-pretreated and (d) rCF-oxidized.

5.3. Conclusion

This work focuses on recovery of carbon fibres from CF/EP prepreg using a combination of a chemical pre-treatment followed by a pyrolysis process. The effectiveness of a pre-treated composite in a 40 wt.% zinc chloride/ethanol pre-treatment agent before the pyrolysis process has been demonstrated. After pre-treatment, some tiny cracks appeared on the surface of CF/EP prepreg potentially due to the synergistic effect of swelling ability of ethanol and coordination ability of and Zn^{2+}. During the pyrolysis process in TGA, the devolatilisation temperature of CF/EP prepreg was lowered by around 30-40 °C and the peak pyrolytic temperature was reduced by 40-50 °C, compared to that of the as-received prepreg. The relatively clean and loose carbon fibres, with some small residues, were recovered from the pre-treated prepreg. This eliminates the need for the extra oxidation process, a common practice in the conventional pyrolysis process for the removal of char residues. The chemical per-treatment process reduces the pyrolysis temperature and oxidation time effectively compared to the conventional pyrolysis process. The rCF-pretreated retains the tensile stiffness similar to virgin carbon fibre and retains 91.80% of the tensile strength. The rCF showed similar chemical elements of C, O and N as the vCF from the XPS analysis, but in varied concentration distribution, and the rCF-pretreated contained negligible composition of Zn and Cl elements. The functional group of rCF-pretreated was closer to the virgin fibre without sizing, while the rCF-oxidized was similar to that of the virgin fibre. The Raman spectroscopy results indicated that the degree of graphitization of both rCF-pretreated and rCF-oxidized slightly decreased, and the degree of graphitization of rCF-pretreated is closer to the vCF. The SEM picture shows some small particles on the surface of the rCF-pretreated, while the rCF-oxidized shows a cleaner surface as for the virgin fibre.

Chapter 6. Microwave pyrolysis process

6.1. Introduction

This chapter reports on carbon fibres extracted from unidirectional CF/EP prepreg using the microwave pyrolysis under a nitrogen atmosphere at temperatures of 450 °C, 550 °C, and 650 °C for 15 minutes. Due to the severe char deposition on the carbon fibre surface, an extra oxidation process was applied in the air in an atmospheric furnace at 550 °C for 30 min. The experimental schema is presented in Table 6-1. The thermal properties of prepreg were tested using TGA in N_2 and air. The mechanical properties, surface morphology, and the surface element of recovered fibres were characterized using a single fibre tensile tester, SEM, and XPS. Virgin fibres were also included. The sample code of testing materials is included in Table 6-1 . The component and composition of pyrolytic gas and oil from resin at different temperatures were investigated using GC and GCMS. The results are discussed in the following sections.

Table 6-1 Experiment schema and test sample code.

Experiment code	Microwave Pyrolysis		Thermal Oxidation	
	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)
E1	450	15	550	30
E2	550	15	550	30
E3	650	15	550	30
Test sample code				
vCF	Virgin Carbon Fibre			
rCF-450	Recycled Carbon Fibre collected from E1			
rCF-550	Recycled Carbon Fibre collected from E2			
rCF-650	Recycled Carbon Fibre collected from E3			

6.2. Results and discussions

6.2.1. Thermal behaviour of carbon fibre prepreg

The thermal behaviour of the cured prepreg under oxygen and nitrogen was studied using thermogravimetric analysis. Figure 6-1 shows the thermal degradation curve of CF/EP prepreg in nitrogen. After an inappreciable drop at the initial heating stage, there is a single sharp drop in mass before reaching the plateau region. The negligible drop was mainly due to moisture loss, and the degradation of the epoxy matrix provides a sharp loss in mass. The mass loss at 1100 °C was 32.75 wt.%, lower than the nominal resin content of the prepreg (37 wt.%). This difference was attributed to the pyrolytic char formed during the degradation of aromatic and cyclic structure in the epoxy resin (Lyon, 1998), also indicating that the clean fibre cannot be extracted directly by pyrolysis in nitrogen (Meyer et al., 2009). Figure 6-2 shows the thermal behaviour of CF/EP prepreg heating in air. Three main stages in the mass loss were event. The mass losses associated with each phase were 21 wt.%, 16 wt.% and 61 wt.%, respectively. The final residue mass approaches zero, which indicated that the composite can be degraded completely in the air. The three corresponding peaks occurred in the ranges (a) 250 °C-450 °C (b) 450 °C-650 °C and (c) 650° C-900 °C.

These three stages respectively represent (a) oxidation of the epoxy resin, (b) oxidation of the pyrolytic carbon and (c) oxidation of carbon fibre (Jiang et al., 2007). The most active degradation process of epoxy resin in air happened at around 415 °C, which consisted of the pyrolysis temperature in a nitrogen atmosphere. The pyrolytic char was oxidized between 450 °C and 650 °C, and the most intense temperature of char oxidation was around 550 °C. After 650 °C, carbon fibre was oxidized until the residual mass almost dropped to 0 wt.% at 950 °C. Based on the TGA result, temperature is the crucial factor, in eliminating pyrolytic carbon whilst minimising fibre oxidation. To investigate the temperature effect on resin degradation and quality of recycled carbon, the microwave pyrolysis temperature was set at 450 °C, 550 °C and 650 °C. According to the TGA result, the most suitable char oxidation temperature was set at 550 °C.

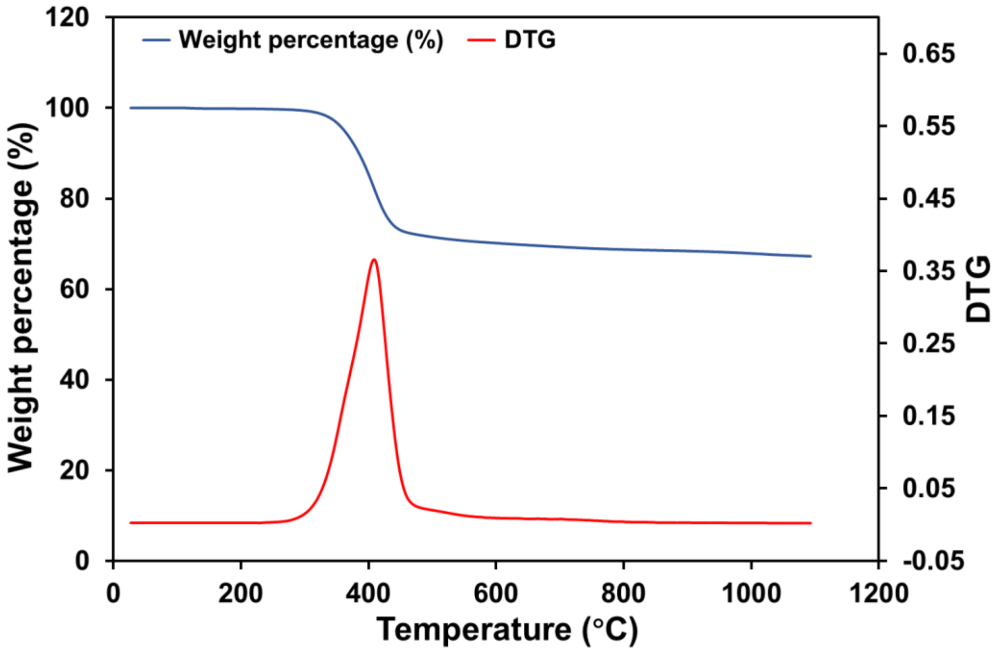


Figure 6-1 Thermal behaviour of CF/EP prepreg in nitrogen.

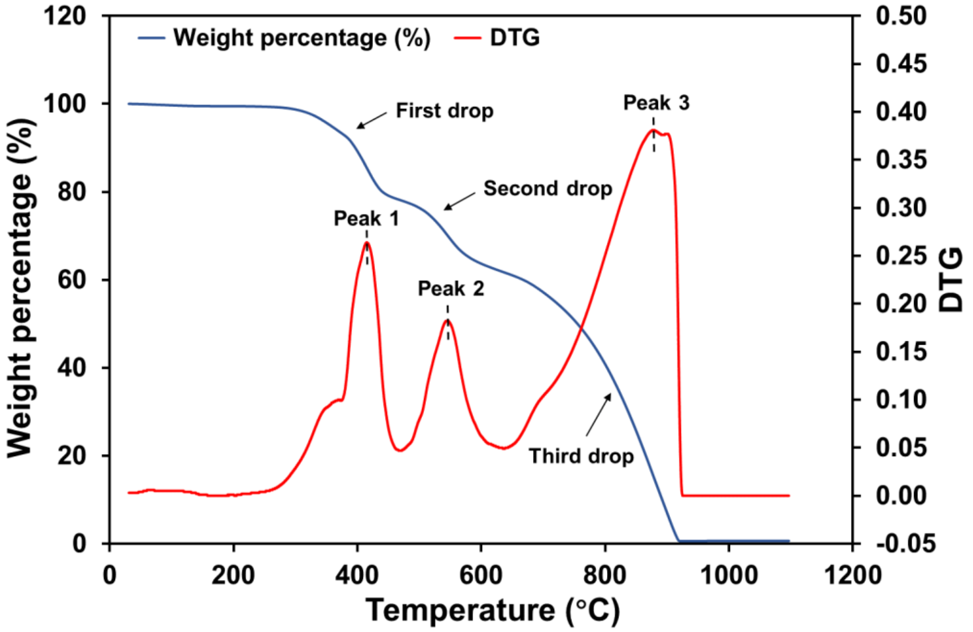


Figure 6-2 Thermal behaviour of CF/EP prepreg in air.

6.2.2. Yield of pyrolytic product

Since the carbon fibres are not affected by the microwave pyrolysis in N_2, the pyrolyzed product arises from the resin matrix. The solid residue consists of stable carbon fibre and pyrolytic char. Char formation in pyrolysis of polymeric materials has been well demonstrated in previous studies (Buekens and Huang, 1998; Grittner et al., 1993). The char content was calculated by the difference of solid residue and carbon fibre content. The pyrolytic solid residue, liquid and gas yield obtained at different microwave pyrolysis temperature are listed in Table 6-2. The temperature had a positive effect in reducing the char content as well as increasing the yield of oils and gaseous products. When the temperature was raised from 450 °C to 650 °C, the char formation reduced from 6.1 wt.% to 2.9 wt.%, with a corresponding increase in liquid and gas yield. The char reduction due to the release of inner volatiles and the availability of more thermal energy to break down stronger organic bonds in the matrices at higher temperature (Zhang et al., 2016). Increasing gas yields are frequently associated with increased cracking of volatiles at higher temperatures, which attributed to the thermal cracking of C–C bonds produced at higher temperatures (López et al., 2011) and conversion of epoxy into volatiles, such as hydrogen, methane, carbon monoxide and carbon dioxide (Naqvi et al., 2018). A similar trend has been reported in pyrolysis of pure epoxy (Cunliffe et al., 2003a) and thermolysis of carbon fibre reinforced polybenzoxazine resin composite (López et al., 2013), with char yields decreased and corresponding oil and gas yields increased when the temperature increases. Also, other pyrolysis studies on large particle coal (Valdés and Chejne, 2018), biomass (Fagbemi et al., 2001) and municipal solid waste (Anh et al., 2008), reported that increasing temperature led to less char formation. In this context, higher microwave pyrolysis temperature led to the lower char residues on the recovered carbon fibre surface.

Table 6-2 Mass balance of microwave pyrolysis of carbon fibre reinforced epoxy prepreg.

Temperature (°C)	Solid residue (wt.%)	Char* (wt.%)	Oil (wt.%)	Gas (wt.%)
450	69.12	6.12	17.71	13.16
550	67.55	4.55	19.15	13.30
650	65.93	2.93	20.28	13.79

*Char is calculated by solid residue minus fibre weight fraction.

6.2.3. Mechanical properties of recycled fibres

Fibre tensile strength was tested to investigate any structural damage to the fibres during thermal processing. The result of the single fibre tensile test was analysed using the Weibull statistical approach. The mechanical properties of fibre pyrolyzed at different temperature are listed in Table 6-3. The virgin carbon fibre also included as the benchmarking.

Table 6-3 The tensile properties of virgin and recycled carbon fibre.

	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile strength retention (%)
vCF	4670	212.22	100 %
rCF-450	4078	201.23	87.3 %
rCF-550	3870	203.57	82.9 %
rCF-650	3766	196.96	80.6 %

The Weibull tensile strength and tensile modulus of virgin carbon fibre are 4670 MPa and 212.22 GPa, which approach to the manufacture’s data, i.e. 4900 MPa for tensile strength and 230 GPa for tensile modulus. The tensile strength of the recycled fibre was lower than that of the virgin fibre whilst the tensile modulus showed no significant change. When the pyrolysis temperature was raised from 450 °C to 650 °C, the tensile strength of recovered fibre lost 13-20 % and the tensile modulus showed a slight decrease or nearly the same as that of the virgin carbon fibre. Degradation in tensile strength was attributed to the pyrolysis temperature increase and char residue oxidation (Bai et al., 2010). The extra oxidation stage would clearly reduce fibre diameter, further, to affect the fibre tensile properties. From the above calculation, the char content of rCF-450 was higher than that of rCF-550 and rCF-650. After the oxidation, the rCF-450 has the highest tensile strength, which may be explained as the char protective effect on the fibre surface. rCF-650 suffered more severe oxidation due to the less char residue, which results in lower tensile strength. By comparison, the earlier study of Lester et al. (2004) yielded around 80 % tensile strength with a negligible change in tensile modulus. Obunai et al. (2015) also reported that the tensile strength of fibre extracted from microwave heating in argon was similar to that of virgin fibres. Decomposition of CF/EP laminates using microwave heating for 180 min at 600 W showed that the tensile strength of recycled carbon fibre was only 24 % of that of the virgin carbon fibre (Emmerich and Kuppinger, 2014). Pimenta and Pinho (2012) reported a 21 % and 84 % reduction in fibre diameter and tensile properties respectively in the research of the effect of pyrolysis condition on fibre mechanical properties. A similar reduction in tensile strength due to the extra oxidation of carbon fibre at high temperature has been reported by López et al. (2013) and Ma et al. (2020). Here, the retention of 90% strength, confirms the technical feasibility of recycling high quality carbon fibre via microwave pyrolysis (Burn et al., 2016).

6.2.4. Surface morphology of recycled fibres

The surface morphologies of the char coated carbon fibre after pyrolysis and final recycled carbon fibre after the oxidation process are shown in Figure 6-3 and Figure 6-4. Figure 6-3 shows that the quantity of char retained on the fibre surface varies with temperature and as the pyrolysis temperature rises, so the fibres are cleaner. This is consistent with the above calculations of char yield, which demonstrated that char reduced with the increase in temperature. As shown in Figure 6-4, the recycled fibres obtained at 450 °C, 550 °C and 650 °C are relatively clean and with an unbroken surface morphology after the char oxidation. A small amount of char and ash (Song et al., 2017) are visible on the 450 °C sample. Some small pits appear on the fibre recycled at 650 °C, which are attributed to oxidation. The 550 °C specimens are the closest in appearance to the virgin fibre. The SEM micrographs highlight the significant and effectiveness of char oxidation process for recovery the clean carbon fibre and help to explain the tensile strength decrease of fibre as the pyrolysis temperature increase. Similar observation was reported by Mazzocchetti et al.(2018), they observed pyrolytic carbon residue on the surface of recycled carbon fibre pyrolyzed in N_2. After the oxidation in air, the recycled fibres showed a complete and relative clean surface. Hao et al. (2020) investigated the effect of pyrolysis temperature and heating rate on the char derived from epoxy prepreg. They reported that the pyrolytic char content decreased when temperature and heating rate increased.

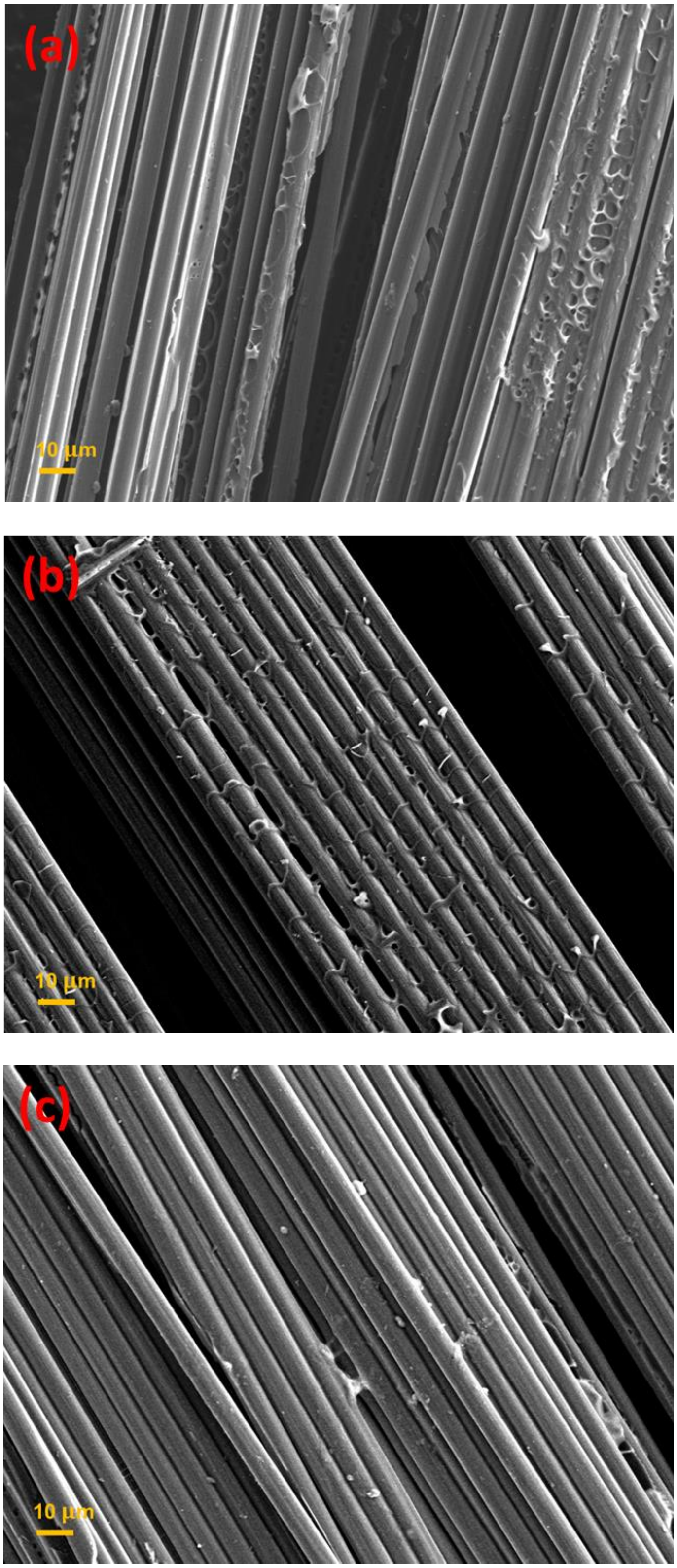


Figure 6-3 The surface morphology of char coated carbon fibre after microwave pyrolysis at (a) 450 °C, (b) 550 °C and (c) 650 °C.

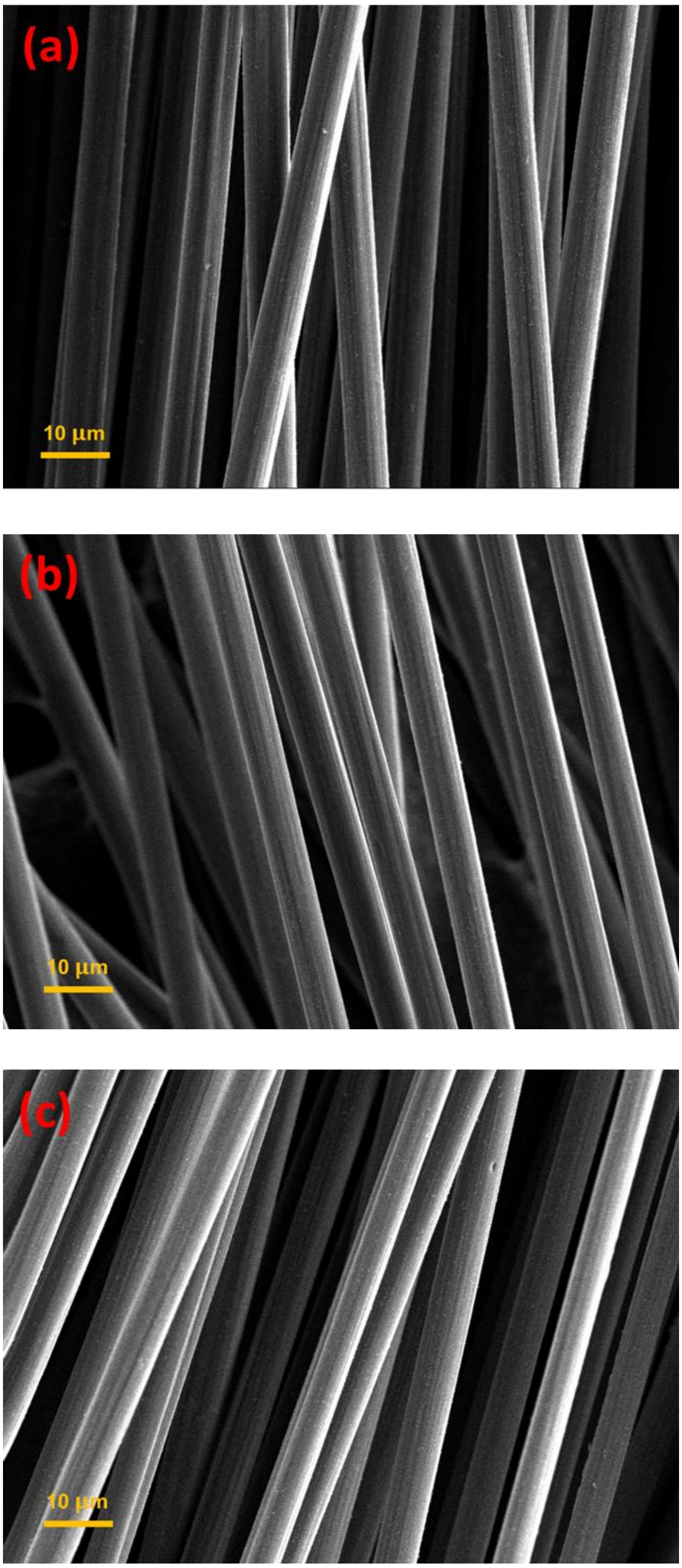


Figure 6-4 the surface morphology of recycled carbon fibre after oxidation at (a) 450 °C (b) 550 °C and (c) 650 °C.

6.2.5. Surface element and functional groups of recycled fibres

The atomic elemental information and functional groups on the carbon fibre surface were evaluated using XPS. The element and composition on carbon fibre surfaces were analysed from the wide scan spectra (Figure 6-5) by CasaXPS software and listed in Table 6-5. As shown in Figure 6-5, two main peaks represent the major element on the virgin carbon fibre surface, which is carbon (280-292 eV) and oxygen (525-540 eV) element (Song et al., 2017). Trace amounts of nitrogen and silicon were also detected potentially came from the carbon fibre manufacturing process (Jiang et al., 2008). The carbon, oxygen and nitrogen composition of the virgin carbon fibre is 77.10 %, 22.39 % and 0.51 % respectively. The O/C ratio of the commercial epoxy resin is 0.2 (Yip et al., 2002) and virgin fibre is 0.29, which approximate to the O/C ratio of commercial epoxy resin and suggested that the virgin carbon fibre surface was epoxy sized. The recycled carbon fibre shows a similar composition of carbon and oxygen in a variable proportion and higher proportion of nitrogen then vCF. The increase in nitrogen probably due to the incomplete carbonization of the precursor or surface treatments at the end of the fibre manufacturing process (Cazeneuve et al., 1990). In this case, the removal of sizing on recycled carbon fibre was indicated by the increase of nitrogen proportion. The presence of C reduced while that of the O increased gradually for recycled fibre when the pyrolysis temperature increased from 450 °C to 650 °C. The atomic O/C ratio is a quantitative measurement of oxygen-containing functional groups on carbon fibres surface and a good indicator of the effective surface area of chemical bonding between carbon fibres and resins (Yip et al., 2002). The increasing of O/C ratio of rCF indicated that some oxygen-containing functional groups were introduced on the recycled carbon fibre surface, which improves the surface activity and enhances for the chemical adhesion of recycled CF and polymer matrix (Yue et al., 1999). The O/C ratio of rCF increased from 0.253 to 0.331 when the pyrolysis temperature increased from 450 °C to 650 °C, indicating that higher pyrolysis temperature promotes more oxygen-contained group on the fibre surface. A similar increase in the O/C ratio of rCF has been reported by other researchers (Kim et al., 2017; López et al., 2013; Song et al., 2017).

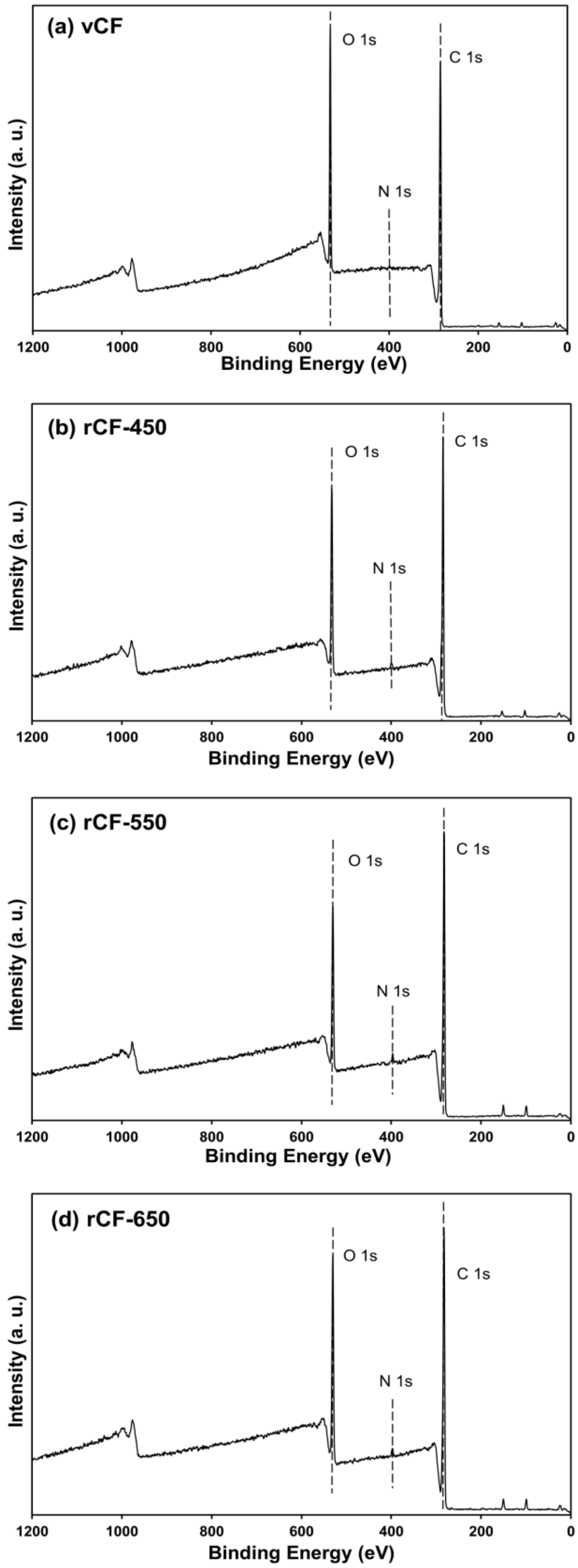


Figure 6-5 XPS wide scan spectra of (a) vCF, (b) rCF-450, (c) rCF-550 and (d) rCF-650.

Table 6-4 The elemental concentration on the carbon fibre surface determined by XPS.

	Element composition (%)			
Samples	C 1s	O 1s	N 1s	O 1s/C 1s
vCF	77.10	22.39	0.51	0.29
rCF - 450	78.05	19.77	0.97	0.253
rCF - 550	75.53	23.02	1.45	0.305
rCF - 650	74.12	24.57	1.31	0.331

The functional groups on the fibre surface were determined in C 1s high-resolution narrow spectrum. The C 1s narrow spectrum was curve-fitted of component peaks of C–C (284.4 eV) (Terzyk, 2001), C-O- or C-OH (285.4-286.3) (Terzyk, 2001) and C=O or COO- (287.2-289.3) (Terzyk, 2001) according to the binding energy. The fittings are shown in Figure 6-6 and the content of the functional group is listed in Table 6-5. The virgin carbon fibres have the highest proportion of C-O- group due to the epoxy sizing on the fibre surface, which is consistent with the result of O/C ratio. The recycled carbon fibres have similar functional groups as virgin fibre but in variable composition at different pyrolysis temperature. The C-C is the main functional group of rCF, while the oxygen-containing group (C-O-, COO-) of rCF is higher than that of vCF. The increased oxygen-containing group indicated that the chemical reaction between carbon fibre and oxygen happened during the resin decomposition and char oxidation process. The rCF-550 has a similar C-C bond content as the virgin fibre. The decrease in C-C of rCF-450 and rCF-650 may be due to the uncomplete char removal and over oxidization, respectively. The rCF-650 have the most abundant oxygen-containing group, which is a possible reason for explaining the mechanical properties decrease of rCF-650. The increase in oxygen-containing groups of rCFs caused by recycling has been reported by Song et al. (2017), which indicated the occurrence of the chemical reaction between carbon fibres and oxygen. Wu et al. (2019) successfully reclaimed carbon fibre from pyrolysis in both molten $ZnCl_2$ and air. They reported that the increase in the content of C=O and C–OH of recycled carbon fibre is due to the mild oxidation in air. Yang et al. (2015) also demonstrated that C-C reacted with oxygen to form the oxygen-containing groups when increasing the temperature and oxygen concentration in the mixed gas atmosphere. The rCFs in this work performed the similar chemical bonding with virgin carbon fibres, and therefore the rCFs would also be suitable for bonding to a polymer matrix in a composite.

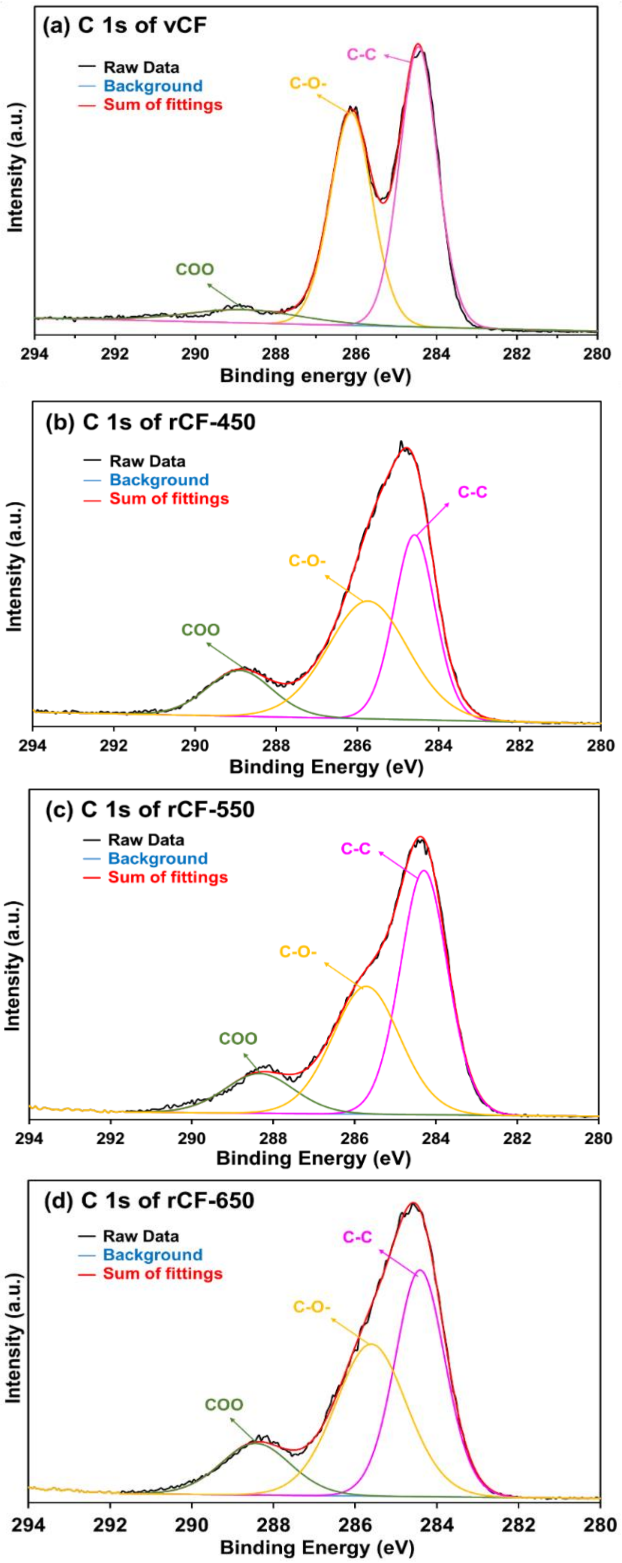


Figure 6-6 C 1s high resolution spectrum of (a)vCF, (b) rCF-450, (c) rCF-550 and (d) rCF-650.

Table 6-5 The relative contents of functional groups on carbon fibre surface determined by XPS.

Samples	Functional group (%)		
	C-C	C-O-	COO-
	284.6 eV	285.4-286.3 eV	287.2-289.3 eV
	(Terzyk, 2001)	(Terzyk, 2001)	(Terzyk, 2001)
vCF	50.46	42.52	7.02
rCF-450	45.61	41.37	13.02
rCF-550	50.37	37.67	11.96
rCF-650	44.01	42.04	13.95

6.2.6. Composition of pyrolytic gas

The formation of gas production is a consequence of devolatilization, cracking reaction at high temperatures and the reactions between the species formed during pyrolysis (Domínguez et al., 2007; Ferrera-Lorenzo et al., 2014). The gas products from microwave pyrolysis of carbon fibre/epoxy prepreg at different temperature were analysed using GC analysis and the results are listed in Table 6-6. The main components are CO (16.64 vol.%-43.91 vol.%), H_2 (11.66 vol.%-47.04 vol.%), CO_2 (26.84 vol.%-42.03 vol.%) and CH_4 (0.51 vol.%-822 vol.%). At the same time, a small amount of C_2H_6, C_2H_4 and C_3H_8 were also produced. As the temperature rose to 650 °C, the H_2 concentration increased significantly from 11.66 vol.% to 47.04 vol.% while there was a fluctuating reduction for the proportions of CO_2, H_2 and CH_4.

Figure 6-7 shows the chemical structure of the most common used epoxy resin, i.e. bisphenol-A type epoxy resin (Li et al., 2016). It can be seen that the structure contains the ether bonds (C-O-C) and epoxide groups. The presence of CO and CO_2 is due to cracking of oxygen heterocycle and ether bonds (C-O-C) in the polymer structure, and the hydrocarbon is produced by the breakdown of alkyl group in epoxy polymer chain (Wei et al., 2006). A higher pyrolysis temperature favours the cracking of the volatiles. H_2 is produced by the dehydrogenation reactions of char and oil, such as aromatization, condensation, and alkene formation (Yang et al., 2006). Cunliffe et al. (2003b) reported that the increases of CO in the gaseous product of pyrolysis of pure epoxy at the temperature range of 400 °C to 500 °C and Yang et al. (2015) analysed that major gas component of pyrolysis of carbon fibre/epoxy composite was CO, CH_4, H_2 and CO_2. Other researchers also reported that the major gas product component is CO_2 (up to 22.71%) and CO (up to 13.29%) obtained in PET pyrolysis (Williams and Williams, 1999). Torres et al. (2000) pyrolyzed SMC composite with a thermoset resin and reported that the gas product is rich in CO (56–68 vol.%) and CO_2 (22–34 vol.%).

Table 6-6 The gas product from microwave pyrolysis of CF/EP prepreg.

Gas	Pyrolysis Temperature (°C)		
(vol.%)	450	550	650
CO	39.68	42.03	26.84
H_2	11.66	32.18	47.04
CO_2	43.91	16.64	25.56
CH_4	4.55	8.22	0.51
C_2H_6	0.12	0.57	0.03
C_2H_4	0.06	0.25	0.02
C_3H_8	0.02	0.12	0.00

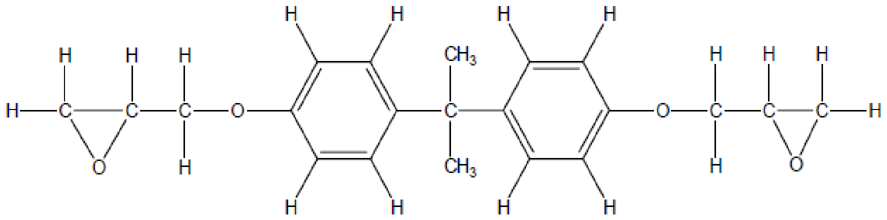


Figure 6-7 Chemical structure of Bisphenol-A Epoxy resin (Li et al., 2016).

6.2.7. Composition of pyrolytic oil

A semi-quantitative analysis on the relative percentage of the chromatographic area of each compound was performed to determine the percentage of major compounds present in the pyrolytic oil at different temperatures. Table 6-7 lists the GCMS result of pyrolytic oil from carbon fibre epoxy composite at 450 °C, 550 °C and 650 °C. The components are classified as Phenols, Aromatics, Hydrocarbons, Amines, Acid and other components and the major compounds of each group are shown. For the liquid products, the main product is phenols, aromatics and hydrocarbons, which due to the breakdown of C-C, C-O bonding in the chemical structure of epoxy resin (showed in Figure 6-7) in the high temperature pyrolysis process. When the temperature was raised to 650 °C, the phenols increased around 20 wt.% which indicated the phenols or benzene derivatives are cracked at high pyrolysis temperatures while the aromatics, hydrocarbons and other component reduced. Epoxy resins are associated with aromatic compounds (Akesson et al., 2013). Amines were detected in the oil, reducing with higher temperatures which due to the bisphenol A and amine compounds with two aromatic rings are relatively difficult to remove in oil products (Yang et al., 2015). Cunliffe and Williams (2003b) pyrolyzed glass fibre reinforced polyester composite and found aromatic compounds in the pyrolysis oil. Torres et al. (2000) pyrolyzed SMC composites at temperatures ranging from 300 to 700 °C and found that the pyrolysis oils contained 64-68 % aromatic compounds. But as shown in Table 6-7, the phenols are the main product. Similar liquid products (phenols, aromatics and their derivates) of pyrolysis of carbon fibre/epoxy resin composite reported by Yang et al. (2015). Pyrolytic oils can be used as a fuel or fuel components, or conversion of the oil into synthesis gas ($CO + H_2$) as it is widely used in the chemical industry and applications (Akesson et al., 2013).

Table 6-7 The oil product composition (wt.%) from microwave pyrolysis of CF/EP prepreg.

Classification	Major compounds	Temperature (°C)		
		450	550	650
Phenols	phenol phenol, 2-methyl Phenol, 3-ethyl p-Cumenol p-Croesl etc.	51.31	53.10	71.69
Aromatics	Benzene Benzene, 1-ethyl-4-methoxy Benzene, 1,3-bis(1,1-dimethylethyl) etc.	16.34	11.57	4.90
Hydrocarbons	Hexane, 2,3,4-trimethyl Dodecane, 4,9-dipropyl Heptadecane, 3-methyl Eicosane etc.	12.19	3.82	5.93
Amines	Benzenamine, 3,4-dichloro Benzenediamine, 4-methyl etc.	5.03	9.89	0.97
Acid	Benzoic acid, 2-(4methylphenoxy) Diphenolic acid etc.	3.04	7.01	0.00
Others	Some Ethanols, Ethers etc.	11.29	14.62	16.53

6.3. Conclusion

In this work, carbon fibres were extracted from cured CF/EP prepreg successfully under microwave pyrolysis process at the temperature of 450 °C, 550 °C and 650 °C. Increasing temperature has a positive effect on reducing the char residue on fibre surface as well as increasing the yield of oil and gas products. The carbon fibre recovered at 450 °C showed the highest tensile strength compared to that of other groups due to the char protective effect. There was no significant change in tensile modulus for all extracted fibre. Some pyrolytic char residue was observed on the recovered fibre surface after microwave pyrolysis. After the oxidation process, the recycled carbon fibre showed a relatively clean and complete surface. XPS indicated that the O/C element ratio increased for the recycled carbon fibre, and the oxygen-containing group increased after the recycling process. For the resin decomposition product, the main component was H_2, CO and CO_2 in gaseous phase product and the major liquid component were phenols and aromatics. In summary, microwave pyrolysis revealed the potential to recover both high-quality fibre as well as valuable chemical feedstock and to save thermal energy.

Chapter 7 Conclusions and future work

7.1. Novelty points

This research aims to recycle the high-quality carbon fibre from waste carbon fibre composite using the pyrolysis technologies. The novelty points of this research are:

- Optimize the industrial conventional pyrolysis process to achieve the lowest char formation, further to save the thermal energy for char oxidation.
- Innovatively propose the hybrid recycling method which involves a chemical pre-treatment process before pyrolysis at optimal condition to recycle the carbon fibre direct from pyrolysis stage.
- Innovatively apply the microwave heating to pyrolysis process to reduce the processing time and to potentially save the thermal energy

7.2. Conclusions

The increasing use of carbon fibre reinforced plastic composite in various industries inevitably leads to a large amount of waste. This research aims to optimize and develop different pyrolysis technologies from the respect of char elimination so that a higher quality carbon fibre can be recovered with the potential for energy and cost savings.

The utilization of a faster heating rate and a high pyrolysis temperature are effective in reducing char formation in conventional pyrolysis process on epoxy and phenolic resins. In addition, this combination reduces consumption of inner gas for purging of volatiles. Also, the fast heating rate increases the char oxidation reactivities; such higher reactivity leads to a quicker oxidation at a lower temperature. Furthermore, the chemical pre-treatment applied before the optimized conventional pyrolysis effectively reduces the degradation temperature of the resin, the intensity of pyrolysis reaction, and oxidation time of char, and the recovery of higher quality carbon fibres from this hybrid process. In addition, a shorter time of degradation of resin is achieved due to the special heating nature of microwave pyrolysis. In summary, the optimization and the use of chemical pre-treatment, compared to conventional pyrolysis, results in benefits from shortening the time and lowering the temperature of oxidation, and potentially eliminates this extra process in the industrial conventional pyrolysis recycling process. Microwave heating provides a possible solution which can reduce the degradation time of resin in the waste composite. These technologies demonstrate the potential capability of recovering high quality carbon fibre with relatively low energy use and cost.

7.3. Future work

7.3.1. Conventional pyrolysis

- Optimization of other conventional pyrolysis parameters to further promote char reduction is worth pursuing, such as gas atmosphere, dwell time and pressure, as these parameters have the potential in affecting resin devolatilization behaviour.
- The resin degradation mechanism during pyrolysis treatment should be further investigated to provide a better insight into the relationship between the resin degradation rate and different process parameters. This can be achieved by using an online characterization method, such as TG-FTIR or TG-GC.
- Other future investigation includes an investigation on the effect of catalyst on conventional pyrolytic products distribution and composition.

7.3.2. The hybrid recycling method

- For the chemical pre-treatment approach, the usage of $ZnCl_2$/ethanol solution can be optimised by using a design of experimental approach to identify the optimum composition to further reduce char formation.
- Other Lewis acids or organic solvent systems can be considered

as an alternative for the $ZnCl_2$/ethanol solution and the future study should be expanded to include different type of epoxy systems or other thermosetting resins because the effectiveness of chemical pre-treatment is likely to be dependent on the resin type and chemical structure. Therefore, another types of Lewis acid, such as $MgCl_2$, $AlCl_3$, and other organic solutions such as Acetic acid, acetone should be analysed.

7.3.3. Microwave pyrolysis method

- The possibility of directly recovering the clean carbon fibre from microwave pyrolysis is also worth studying by applying different or mixed gas atmospheres, such as CO_2, which has relatively inert oxidising capability as compared with air.
- The actual energy consumption of microwave pyrolysis shall be detected, so as to evaluate its efficiency. The reduction in processing time should be further investigated, such as the use of power controlled operating mode and single-mode microwave cavity.

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