

Influence of chemical treatment on the recycling of composites before pyrolysis

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Abstract. Recycling of carbon fibers is one of the upcoming global research topics in composite engineering. This work investigates the influence of chemical treatment on the recovery of carbon fibers from carbon fiber reinforced plastic before pyrolysis. The chemical pretreatment was achieved using a zinc chloride/ethanol solution. The pyrolysis process was conducted in a sliding furnace. The effect of such pre-treatment on thermal degradation behaviour was determined by a thermogravimetric analyser (TGA). An original sample was also investigated for benchmarking. After the thermal pyrolysis process, the fiber tensile properties were measured using a single fiber tester. The surface functional groups and graphitization degree recovered carbon fiber were characterized using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The surface morphology of recycled carbon fibers was investigated by SEM. Pristine carbon fibers were also included in the study for benchmarking. During the pyrolysis process, the devolatilisation temperature of the pre-impregnated prepreg reduced by around 40-50°C and the peak temperature was 40-50°C lower compared to that of the original prepreg. The chemical pre-treatment process reduces the pyrolysis temperature compared to the conventional pyrolysis process. After pyrolysis in nitrogen with a small amount of air, loose carbon fibers were recovered, and their surface was clean. The similar surface functional groups and the decrease of degree of graphitization were detected on the recycled carbon fiber.

Keywords: Carbon Fiber; Recycling; Chemical Treatment; Pyrolysis

1. Introduction

Carbon fiber reinforced plastic (CFRP) composites have been widely used in many industrial fields such as the automotive and aviation industry due to their impressive properties of low weight, high strength, and high stiffness, but a large number of waste composites are inevitably generated in the manufacturing process and at the end of their service life [1]. The high specific performance serves as the driving force to aid the epoxy-based CFRP to dominate the composite markets, meeting the consumer demands [2]. On the other hand, it poses a great threat to the environment at the end of its service life. Industries face a significant challenge in recycling these composites mainly due to their irreversible cross-linked structure of the epoxy matrix. Considering the environmental and economic impact, recycling has become one of the top priorities in composite industries, a variety of recycling technologies such as fluidized bed, pyrolysis, and solvolysis have been studied intensely across the globe [3]. Pyrolysis treats composite waste at high temperatures in an inert environment to convert the



thermoset matrix into volatiles and char. The volatiles can potentially be further processed for energy recovery or being used as a feedstock for the manufacture of lower molecular weight chemicals. The char, however, remains on the surface of the recovered carbon fiber. The amount of char residue depends on the resin chemical molecular structure, for example, the presence of aromatic and other cyclic structures in epoxy resin structure promote the char formation during the pyrolysis process [4]. An extra oxidation process, at a temperature ranging from 600-650 °C, is thus necessary for char removal so that clean carbon fiber can be recovered. However, it has been reported that the mechanical performance of the recovered carbon fiber can be degraded by the oxidation process [5].

In previous research, strong acid[6] or alkali solution[7] was used in dissolving the epoxy matrix in the chemical recycling approach. Recently, the milder environment has been reported from the use of Lewis acids, such as $ZnCl_2$ and magnesium chloride ($MgCl_2$) in solvents like water and ethanol. A CFRP waste ($T_g > 210$ °C) was effectively decomposed in a $ZnCl_2$ /ethanol (20wt.%) catalytic system at 190°C for 5h, the resin degradation ratio was 89.8%[8]. Matthew J. Keith's research demonstrated that $ZnCl_2$ /acetone/water (0.05M) system was an effective catalyst to dissolve more than 94 % epoxy resin and the process could be shortened with higher temperature, i.e. from 1.5 hours to 45 minutes by increasing temperature from 290 °C to 300 °C [9]. Furthermore, the epoxy composites could be completely dissolved in a molten $ZnCl_2$ at 360 °C in 80 min under standard pressure, due to the fracture of the C–N bonds in the epoxy matrix by the catalytic action of Zn^{2+} ions[10].

The novelty of this paper is to apply a chemical pretreatment process before the conventional pyrolysis to initiate the breakdown of the cross-linked structure of the epoxy matrix before subjecting the composite to the conventional pyrolysis process, further to reduce the resin degradation temperature and reduce the negative impact the oxidation process causes on the recovered carbon fiber. The zinc chloride ($ZnCl_2$) /ethanol pretreatment system was used to pre-immersed the experimental specimens. First, a TGA unit 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. Then, tensile properties of the fibers recovered from these samples were measured via a single fiber tester. The surface morphology of recycled carbon fibers was investigated by SEM. The surface functional groups and graphitization degree recovered carbon fiber were characterized by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

2. Materials and methods

2.1. Materials

Unidirectional carbon fiber reinforced epoxy prepreg made of Toray@ T700s-12K carbon fiber and epoxy resin was provided by Aojing@ Composite Company, Shanghai, China. The epoxy resin content was 37 wt.%, as provided by the manufacturer's data. The prepreg was first cured at 140°C for 2 hours, then it was cut into a size of 25 mm × 25 mm and immersed in a zinc chloride/ethanol catalyst solution for a chemical pre-treatment process. The analytical reagent zinc chloride powder and analytical reagent ethanol (C_2H_5OH) were provided by Macklin@ chemical technology co. LTD and Hushi@ Lab. Equipment co. LTD in Shanghai, China, respectively.

2.2. Experimental methods

A new hybrid method consists of chemical pre-treatment and conventional pyrolysis was used to recover carbon fiber without extra oxidation. In the chemical pre-treatment process, the CE/EP prepreg was immersed in a catalyst system consists of zinc chloride and ethanol. The experimental set-up is shown in Figure 1. The catalyst solution was prepared by dissolving $ZnCl_2$ powder (40wt.%) 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 20mm × 20mm was 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 volatilization. After the chemical process, the treated sample was washed with distilled water several times, then was dried in an oven at 80 °C for 24 hours. The n the pre-treated sample with the size of 20mm × 20mm

was pyrolyzed at 650 °C for 30 min in a sliding tube furnace (OTF-1200X, shown in Figure 2) 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 collected in an alumina crucible was placed at the left side of the tube. The furnace was started heating in a nitrogen gas with a flow rate of 1000 ml/min. When the temperature of the furnace arrived at 650°C, the extra 1200 ml of compressed air was injected into the tube, and finally, nitrogen gas purged again. The furnace was slid to the sample position and start the pyrolysis when the temperature steadied at 650°C. After pyrolysis for 30 min, the sample was collected when the furnace cooled to room temperature with nitrogen.

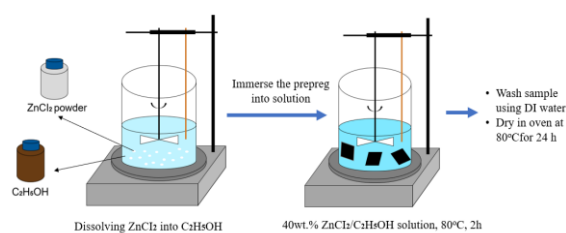


Figure 1. The experimental set-up of the chemical pre-treatment process.

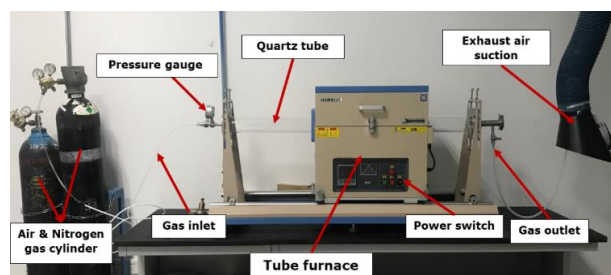


Figure 2. Pyrolysis in the sliding tube furnace.

2.3. Characterizations

2.3.1. Thermal behavior of prepregs. The thermal pyrolysis behavior of original and pre-treated prepreg was determined using a thermogravimetric analyzer (TA@ SDT Q600, USA) from room temperature to 650°C with the heating rate of 200°C/min in a nitrogen atmosphere. The devolatilised temperature of carbon fiber prepreg was determined from the mass loss curve (TG) and the first derivative of the mass loss curve (DTG) changes with temperature in nitrogen.

2.3.2. Single fiber tensile strength (SFTT). The tensile strength and modulus of pristine fiber, recycled fiber were determined using a single fiber tensile tester (DiaStron@LEX810/820, UK) and conducted following the ISO 11566 Carbon fiber tensile properties determination standard. For each test, condition 30 individual fibers were tested with the gauge length of 4 mm and load cell of 1N. A constant strain of 0.1 mm/s was applied, and the stress/strain curves of the mounted fibers were recorded automatically to calculate the tensile strengths and modulus.

2.3.3. X-ray photoelectron spectroscopy (XPS). The surface element and functional group of pristine and recycled carbon fiber were determined using an X-ray photoelectron spectrometer (XPS, AXIS ULTRA DLD, Shimadzu, Japan) with an Al K α X-ray source (1486.6eV) 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 analyzed using the CasaXPS software package. The carbon, hydrogen, oxygen and nitrogen traces were scanned. The binding energy was calibrated by referring to the C1s peak at 284.8 eV.

2.3.4. Raman spectroscopy. 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 degree of graphitization of recycled carbon fibers. 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 pristine and recycled carbon fiber were obtained and then analyzed using the Origin software.

2.3.5. Surface electron microscopy (SEM). The surface morphology of recycled fibers was characterized 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. Pristine fibers were also analysed.

2.4. Result and discussion

2.4.1. Thermal behavior of chemical treated prepregs. The thermal pyrolysis behavior of original and pre-treated prepreg in the nitrogen atmosphere was investigated and their mass loss profile over the temperature is shown in Figure 3. For the non-treated sample, after a negligible drop at the early stage of the heating process, then from around 420°C , the profile underwent a sharp drop in mass and reaching a relatively flat plateau region. Then the mass continued to drop when the temperature was maintained at 650°C . The initial negligible drop was mainly due to moisture loss, whilst the conversion of the epoxy matrix into volatiles was attributed to the sharp loss in the 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 non-treated prepreg due to some resin had been removed in the early pre-treatment process. DTG curves of the corresponding samples are shown in Figure 3 and both show only one peak, which can be attributed to the epoxy resin devolatilisation, a fundamental mechanism of the pyrolysis process [11] in the recovery of carbon fiber. 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 [12]. The devolatilisation temperature of the treated composite was reduced by around $30\text{--}40^\circ\text{C}$ and the peak temperature was $40\text{--}50^\circ\text{C}$ lower. Therefore, the chemical pre-treatment process was proved to be effective in reducing the pyrolysis temperature.

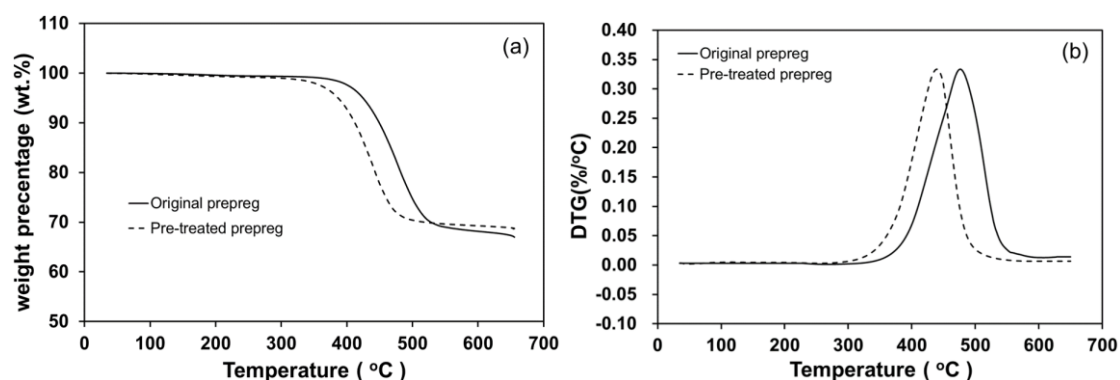


Figure 3. The (a) TG curve and the (b) DTG curve of original and pre-treated prepregs.

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 4(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 4(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 catalyst system; ethanol has a high swelling ability which opens up the epoxy structure in the prepreg to facilitate penetration of the ZnCl_2 catalyst to cause cleaving of C-N bonds in the epoxy's cross-linked 3D structures [8, 13]. The degradation method the catalyst system is shown in Figure 5.

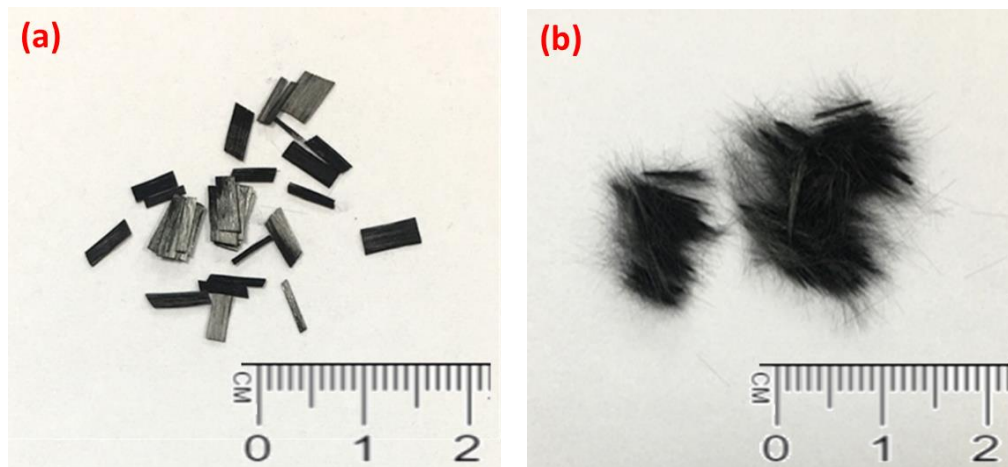


Figure 4. Pyrolysis solid product from (a) original preregs and (b) pre-treated preregs.

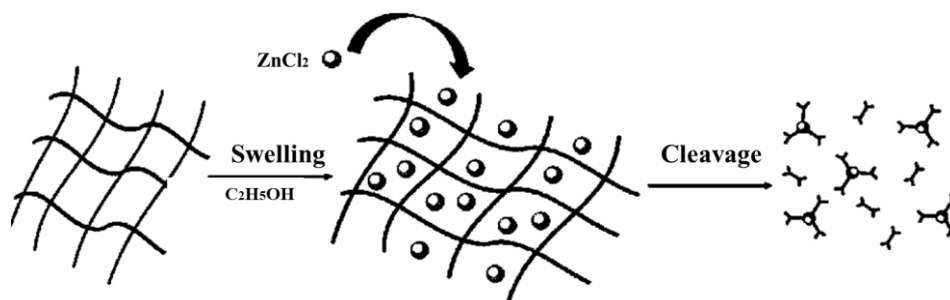


Figure 5. The swelling ability of ethonal and cleavage of $\text{ZnCl}_2/\text{C}_2\text{H}_5\text{OH}$ system[8].

Table 1. The tensile properties pristine carbon fiber (pCF) and recycled carbon fiber (rCF).

Sample	Diameter (micron)	Tensile modulus (GPa)	Tensile strength (MPa)	Tensile strength Retention (%)
pCF	6.82 ± 0.15	210.03 ± 19.43	4670	100
rCF	6.60 ± 0.24	208.15 ± 17.29	4287	91.80

2.4.2. Single fiber tensile test of carbon fiber. Tensile properties of the recovered carbon fibers were characterized by using a single fiber tester and the results are presented in Table 1, which also includes data measured from the pristine carbon fibers. No significant change in the tensile modulus was observed. The average diameter and tensile strength of pristine carbon fiber is 6.82 micron and 4670 MPa. However, after the chemical pre-treatment and pyrolysis process, the diameter and tensile strength decreased by about 3 % and 8 % respectively. Degradation in diameter and tensile strength have been observed from fiber recovered from the previous conventional pyrolysis process [5]. Due to the prolonged oxidation process for char removal at high temperatures, a 28% reduction in tensile strength had been reported by Lopez et al.[14]. Pimenta & Pinho [15] also reported the importance of controlling the pyrolysis condition in avoiding a significant drop in fiber diameter and tensile strength. Up to 21% and 85% reduction in diameter and tensile strength of the recycled carbon fiber (rCF) was reported if an aggressive oxidation condition was used [15]. In this work, rCF retained 91.8% of the

tensile strength of the pristine carbon fiber (pCF) and required no further oxidation process, confirming the benefit of the pre-treatment process.

2.4.3. Surface element analysis of carbon fiber. XPS analysis was used to detect changes in the surface functional groups of the carbon fibers. The XPS wide spectrum of pristine fiber and rCF is showed in Figure 6. . 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 pCF and rCF, representing the main components of the carbon fibers. The surface element composition was analysed and listed in Table 2. The rCF showed a similar composition in C as that of pCF, but a decrease in O element was observed. Also, a negligible composition of Zinc and Chlorine element around 1 to 1.5 at.% was detected which comes from the catalyst system. The vaporization temperature of ZnCl_2 is around 400°C [16], 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 suggested that no further cleaning process is required. Compare with the pCF, the increase in the nitrogen of rCF could be the residue of the PAN precursor in the carbonization process [17], which is that the sizing has been removed through the recycling. The atomic O/C ratio is a quantitative measurement of oxygen-containing functional groups on carbon fibers surface and a good indicator of the effective surface area of chemical bonding between carbon fibers and resins [18]. The O and O/C ratio of rCF were lower than the pCF sized by epoxy which indicated lower surface activity than pCF [19].

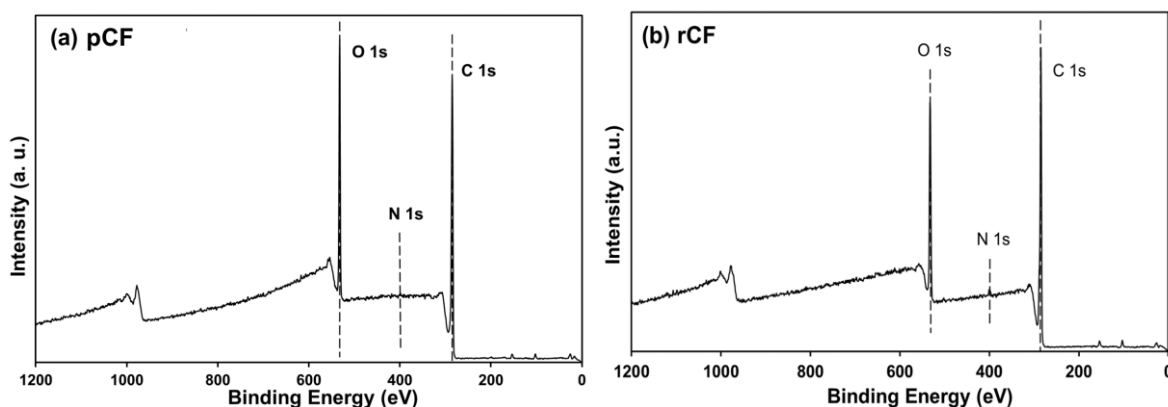


Figure 6. XPS wide spectrum of (a) pCF and (b) rCF.

Table 2. Elemental composite for recycled carbon fiber.

Samples	Element composition (at.%)					
	C 1s	O 1s	N 1s	Zn 2p	Cl 2p	O1s/C1s
pCF	77.10	22.39	0.51	-	-	0.29
rCF	79.76	14.05	3.47	1.36	1.19	0.18

The functional groups on the fiber surface were clarified in C 1s high resolution narrow spectrum. The C 1s narrow spectrum was curve-fitted of component peaks of C–C (284.4 eV)[20], C–O- or C–OH (285.4-286.3) [20] and C=O or COO- (287.2-289.3) [20] according to the binding energy. The fittings are showed in Figure 7 and the relative content of the functional group is listed in Table 3. The surface functional groups of rCFs were similar to that of the pCF but in variable atomic concentration. The C-C bond is the main functional group of both pCF and rCF. The pCF has the highest content of the C-O- or C-OH group probably due to the epoxy sizing. The content of C-C bond of rCF was much higher than that of pCF, which is similar to the pristine fiber after sizing removal [21] in previous study. Previous research reported that the C-O- or C-OH group can be removed in pyrolysis at high temperature [22], so the oxygen-containing group on the surface of rCF indicating the reaction

between carbon fiber with oxygen and the exposure of the fiber without sizing. The C-O- groups were also detected in the surface of rCF, these may come from the residence of resin, which was observed in SEM picture of the rCF. Jiang et al. [23] reported that the C-O- group may be transformed to the C=O- and O-C=O group when carbon fiber began to oxidise when they studied the surface chemistry of rCF. The increase in oxygen-containing groups (C-O-,C=O-) of rCFs indicated the happening of chemical reaction between carbon fibers and oxygen [24]. Wu et al. [10] successfully reclaimed carbon fiber from pyrolysis in both molten $ZnCl_2$ and air. They reported that carbon fiber 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 fiber reclaimed in air due to the mild oxidation. Yamamoto et al. [25] claimed that the C=O- group on the fiber potentially help the fiber wetting property. Moreover, the rCF-pretreated showed a similar surface chemical bonding as the pristine fiber without sizing.

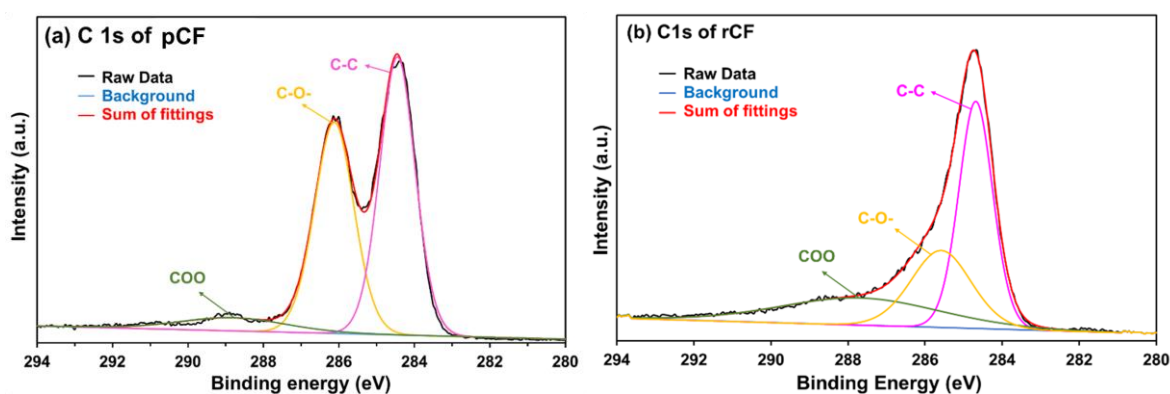


Figure 7. C1 high resolution spectrum of (a) pCF, (b) rCF.

Table 3. The relative contents of functional groups on carbon fiber surface.

Sample	C-C 284.6 eV[20]	C-O-, C-OH 285.4-286.3 eV[20]	C=O, COO- 287.2-289.3 eV [20]
pCF	50.46	42.52	7.02
rCF	70.77	16.34	12.88

2.4.4. Raman spectroscopy of carbon fiber. 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 the graphitization structure of carbon fibers after recycling. Usually, for carbon material, there are two Raman broad band at the frequency around 1350 cm^{-1} and 1580 cm^{-1} , represent the D (disordered) band and G (graphitic) band, respectively. The D band are assigned to the degree of disorder of carbon atom structure, and the G band indicates the graphitic lattice structure [26]. 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 G band (I_G) caused by graphite crystal. Usually, the smaller R value indicates the lower degree of disorder and a higher degree of graphitization of the carbon fibers [27]. In addition, the full widths at half maximum (FWHM) of the band also a parameter to indicate the degree of graphitic and disordered structure, as the bigger FWHM of D band and the G band, more disordered structure [10]. The Raman spectrum of the pristine and recovered carbon fibers at the range from 800 cm^{-1} to 2000 cm^{-1} are shown in Figure 8. From the figures, all Raman spectrum exhibits a similar curve and there are two broad Raman bands located at around 1350 cm^{-1} and 1580 cm^{-1} , which is the D band and the G band, respectively.

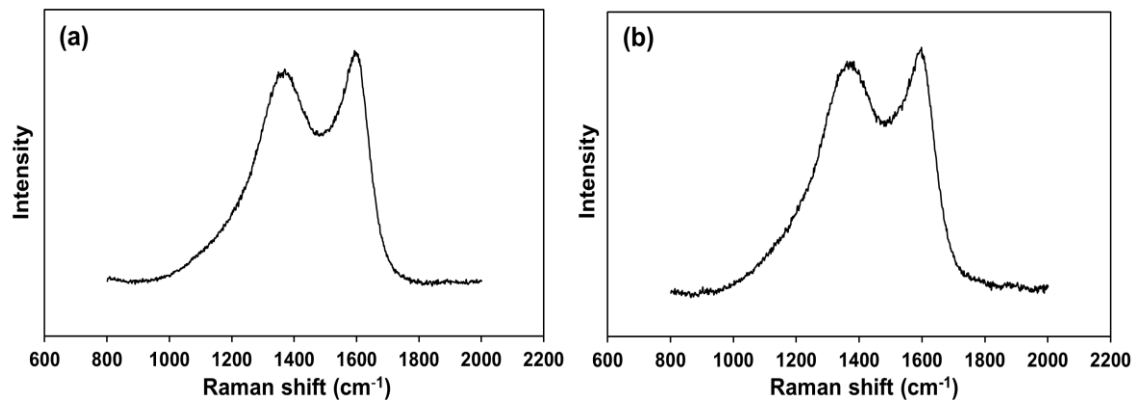


Figure 8. The Raman spectra of (a) pCF and (b) rCF.

Table 4. Raman spectral parameters of the pristine and recovered carbon fiber.

Sample	D band		G band		R
	Raman shift (cm ⁻¹)	FWHM	Raman shift (cm ⁻¹)	FWHM	
pCF	1380.21	291.02	1596.65	106.97	2.94
rCF	1380.62	291.83	1595.76	106.52	3.12

The Gauss peak fitting method was used in the Origin software to determine the Raman parameters, the Raman shift (cm⁻¹), FWHM, and R number were summarized and listed in Table 4. It can be seen from the table that the pristine fiber has the smallest R value of 2.94, indicating that the degree of graphitization of pCF was the highest. Compared to the pCF, the R value of rCF increased by 0.18, indicating that the degree of graphitization of recovered fiber decreased slightly. The FWHM value of D band and G band of pristine fiber is 291.02 and 106.97, respectively. The FWHM value of rCF shows a nearly similar value as that of pristine fiber, reflecting a similar degree of graphitization. A similar result was concluded by Wu et al. [10] using pyrolysis with molten ZnCl₂ and Xu et al. [27] using the chemical recycling with peroxide hydrogen and N,N-dimethylformamide mixture solution. Both reported that the degree of graphitization of the rCFs decreased in comparison with the pristine carbon fiber.

2.4.5. Surface morphology of carbon fiber. Surface morphologies of the rCF were observed via SEM to evaluate the effects of chemical pre-treatment. The comparison was made against pCF and the results are shown in Figure 9. From Figure 9(a), it can be seen that pCF shows a clean, smooth and complete surface. However, Figure 9(b) shows that fiber is covered by a significant amount of char merely after pyrolysis in N₂ without chemical pre-treatment. This phenomenon demonstrated that the importance of char elimination in the application of reuse. Similar continuous and complete fibers were observed from rCF as shown in Figure 9(c), except for the presence of some char particles scatter on the surface. López et al. [28] observed the pyrolytic char on the surface of recycled carbon fiber pyrolyzed in N₂. After the gasification in air, the recycled fibers showed a complete and relatively clean surface. Wu et al. [10] reported the ZnCl₂ has the catalytic effects in resin degradation and good compatibility with the epoxy resin, which promotes the detachment of resin with fiber. Their SEM images showed that fibers recovered in molten ZnCl₂ exhibited a very clean surface. In this work, these SEM pictures emphasized the effectiveness of the pre-treatment process in reducing the char residue.

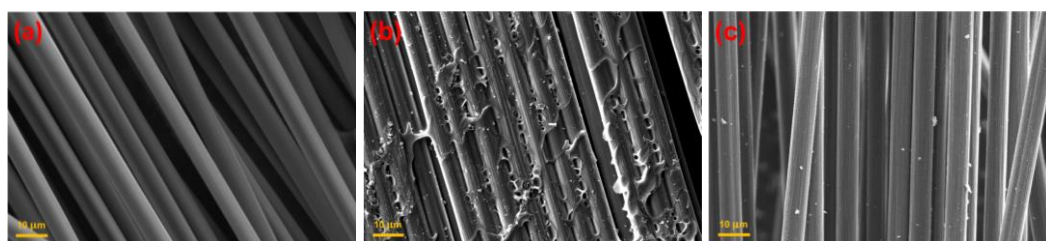


Figure 9. The SEM images of (a)pCF, (b) rCF without pretreatment and (c) rCF-pretreated.

3. Conclusions

This work focuses on the recovery of carbon fibers from CF/EP prepreg using a combination of a chemical pre-treatment followed by a pyrolysis process. The effectiveness of pre-treated composite in the zinc chloride/ethanol catalyst system before the pyrolysis process was demonstrated. During the pyrolysis process in TGA, the devolatilization temperature of CF/EP prepreg lowered by around 30-40°C and the peak pyrolytic temperature was reduced by 40-50°C, compared to that of the original prepreg. The relative clean and loose carbon fibres with some small residues were recovered from the pre-treated prepreg. The chemical pre-treatment process reduced the pyrolysis temperature and oxidation time effectively compared to the conventional pyrolysis process. The rCF retained the similar tensile stiffness to pristine carbon fiber and retained 91.80% of the tensile strength. The rCF showed similar chemical elements of C, O and N as the pCF from the XPS analysis but in various concentration distributions. And the rCF contained negligible composition of Zn and Cl elements. The functional group of rCF was closer to the pristine fibre without sizing. The Raman spectroscopy results indicated that the degree of graphitization of both rCF slightly decreased. The SEM picture showed some small particles on surface of the rCF.

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