RECOVERY OF CARBON FIBER FROM CARBON FIBER REINFORCED POLYMER WASTE VIA PYROLYSIS

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ABSTRACT: The increasing use of carbon fiber reinforced polymer (CFRP) in high end application industry needs for recycling technique to recover the valuable carbon fibers, reduce the waste produced and provide a closed loop for this material. Most CFRP waste have been disposed of in landfills after their expiration of service life, generating environmental problems and potential release of toxic byproducts. This paper examines the recovery of carbon fibers (rCF) via pyrolysis technique by particularly studied the influence of different atmosphere (nitrogen and combination of nitrogen and oxygen) and final heating temperature (550°C, 600°C and 650°C). Pyrolysis held under an inert atmosphere of nitrogen at the heating temperature range from 250 to 420^{0}C was found significance to decompose epoxy resin components. While oxygen atmosphere at higher heating temperature was found needed to achieve a complete elimination of resin from rCF. Pyrolysis at low temperature (550°C) revealed rCF production with clean and uniform spherical shape. Thermogravimetric analysis (TGA) reveal 540°C as final heating temperature that efficiently recover CF. Morphological and structural examination of the rCF was performed via SEM and Raman spectroscopy respectively. The specific heating profile of pyrolysis technique is present to recover valuable CF from complex CFRP.

KEYWORDS: *Recovery; Carbon Fiber; Waste; Pyrolysis*

1.0 INTRODUCTION

Carbon fibers (CF) are the perfect reinforcement material for polymer composites in high end application industry like aerospace due to their advantages of high strength and low weight. The global demand for CF is significantly grow at a rate of 9-12% until 2022 [1-2]. This CFRP complex formulation basically includes an epoxy resin, virgin CF and thermoplastic polymer. Currently, in aerospace composite industry, the CF comes pre-impregnated with resin and forms 'Carbon Prepreg' to ease the manufacturing processes. The Carbon Prepreg in rolls condition is machine-cut using a program into plies with suitable dimensions following the general product shape [3]. However, the excess of the material roll are disposed as wastage and their amount is continuously increased every year together with other forms of waste like production cut-offs and end-of-life components [4-5]. Realizing a significant amount of wastage generated, recycling CF is crucial to bring these rCF back into new composites for secondary industrial application and save the environment through reduction of waste at the landfill.

It was demonstrated that the recycling via thermal decomposition of this complex composite is different from one system to another as it depends on the chemical nature of their components [6-8]. Pyrolysis has been well known due to lower cost process incurred for the recycling of composites, particularly when dealing with high valuable products such as CF based on the research by Pickering [9]. As compared to other methods of recycling, mechanical technique results in a powdered form of carbon after the composites are crushed instead of retain the structure of individual fiber [9]. While, high cost chemical recycling remove the matrix from the CF using different harmful acidic solvents [10]. Optimized and improved low cost pyrolysis utilized heat energy to recover the CF, make it become the most promised method for recycling CFRP [11].

Formerly, Pickering et al. [12] utilized pyrolysis technique in their research work for commercialization scale. However, in order to produce high quality of rCF remaining to the current deficiency of information about the pyrolysis process of lab-scale production primarily for high performance CF composite. A comparative study on the performance of rCF should be extended in order to investigate the effect process pyrolysis and the relationship between the morphology of the rCF and their mechanism of thermal decomposition. The rCF were reported to show a lower strength degradation of typically 20% with preservation of the original stiffness via pyrolysis technique [9].

As far as optimization of rCF has been concerned, disadvantageous mainly due to degradation of the CF surfaces when they were contaminated by char produced during the thermal decomposition process [11]. This decomposition requires a post-treatment in a furnace at higher temperature (>450^{0}C) to burn it which also lead to higher operation cost.

Combination environment of nitrogen followed by oxygen might be better than single pyrolysis environment. Thus, this study aim to further investigate on the perfect and suitable heating profile including final heating temperature and pyrolysis environment to produce quality rCF and completely remove the resin and matrix. Once suitable conditions were achieved, the rCF were analyzed via morphological and chemical approach to further ensure the recovering of 60% CF in CFRP by eliminating completely the complex epoxy resin.

2.0 METHODOLOGY

2.1 Materials

A roll of carbon fiber reinforced polymer (CFRP) prepreg material waste with unidirectional orientation supplied by Composite Technology Research Malaysia Sdn. Bhd. (CTRM) was used for this research. The plain prepreg made of epoxy resin reinforced with carbon fibers (59–60% carbon fibers [by volume] and 40% complex epoxy resin). Type of CFRP is not reported due to a confidential agreement.

2.2 Pyrolysis Process

The 400 g of CFRP was cleaned with distilled water before cut into small size (100mm x 20mm) to be fitted in the ceramic crucible and placed in tube furnace of pyrolysis machine. Different environment (inert gas of nitrogen and nitrogen followed by oxygen) was used at 5cc/mm^3 gas pressure. The tube was vacuumed to avoid the risk of contamination from reactive gases that exist in the air for burning process. The furnace machine was then being programmed with the requirement different temperature (550°C, 600°C and 650°C).

2.3 Morphological Analysis

Morphology behavior of CFRP and rCF were analyzed using scanning electron microscopy (SEM). Structural Analysis of CFRP and rCF were examined via Raman spectroscopy with UniRAM-3500, Micro Raman Mapping, occupied with laser source 532nm & 785nm.

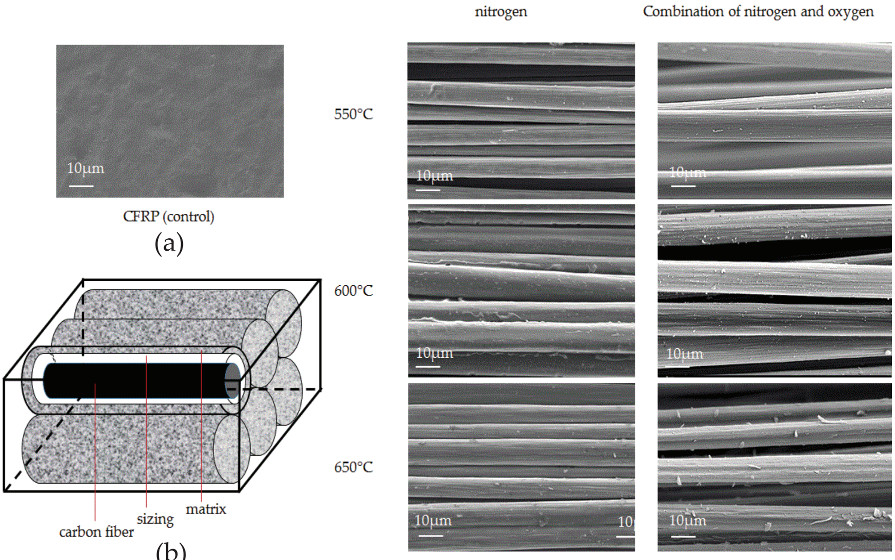
2.4 Thermogravimetric Analysis (TGA)

TGA were carried out on TA instruments TGA 1 brand Mettler Toledo. The balance purge flow was set to 15mL/min and the sample purge flow (nitrogen and oxygen) to 50mL/min. Thin square samples were prepared in a alumina crucible and another empty alumina crucible was used as a reference underwent a heating profile from 250 to 420^{0}C in nitrogen with a heating rate of 5°C/min, followed by holding temperature at 420^{0}C in nitrogen for 30 minutes and heating from 420 to 800^{0}C in oxygen with heating rate of 2^{0}C/min.

3.0 RESULTS AND DISCUSSION

3.1 Morphology Analysis of Decomposed Sample

Figure 1(a) shows the surface analysis of CFRP (control) with the schematic diagram illustration (Figure 1(b)). Figure 1(c) reveals the rCF after pyrolysis at different atmosphere (nitrogen and combination of nitrogen and oxygen) and final heating temperature (550, 600 and 650°C). CFRP (control) before pyrolysis shows a smooth flat surface. Generally, the CRFP is a complex composite contains carbon fiber, sizing and matrix, as illustrated in Figure 1(b).



(a)

(b)

(c)

Figure 1: Surface analysis of (a) CFRP, (b) schematic diagram of CFRP and (c) rCF after thermal decomposition at different atmosphere and final heating temperature

Both pyrolysis process in nitrogen and combination of nitrogen and oxygen atmosphere resulted in rCF that are separated from their epoxy resin. However, further examination reveals different surface properties of recovered CF. CF in nitrogen atmosphere was found still adhere to each other, while combination atmosphere produce visibly individual rCF. Higher final heating temperature (600°C and 650°C) for both atmosphere formed rCF enclosed with many fractured residues and degraded rCF surfaces as compared to lower final heating temperature (550°C) that produced rough and clean surface of rCF.

The devolution of the decomposition reaction is different for both atmospheres. Apparent separation of individual rCF in combination atmosphere suggests both inert pure gases like nitrogen and oxygen are essential in pyrolysis process [8]. In agreement, as reported in [9], the residues removal occurred via pyrolysis in oxygen containing atmosphere. Thermal decomposition in single nitrogen atmosphere always linked to single main decomposition step, while the combination atmosphere mainly involved two main decomposition steps which effectively eliminate the matrix and resin surrounded the CF [9]. The first decomposition step for both atmospheres was attributed to release of small molecules and decomposition of organic epoxy matrix [10]. Decomposition under nitrogen leads to a formation of carbonaceous residue covering the CF due to the carbonization of resin [5]. It means, the resin and sizing can be decomposed in nitrogen atmosphere but left many solid as residue.

Figure 2(a) shows the cross sectional analysis of CFRP (control) with the schematic diagram illustration (Figure 2(b)). Figure 2(c) reveals the rCF after pyrolysis at different atmosphere (nitrogen and combination of nitrogen and oxygen) and final heating temperature (550, 600 and 650°C). RCF in combination atmosphere of nitrogen and oxygen were observed to have more clean and uniform spherical shape, smooth end-surface and less diameter as compared to control due to successful elimination of sizing. However, as the final heating temperature increase (600 and 650°C), the end surfaces of rCF is degraded and formed hollow structure. The combination of atmosphere at low temperature (550°C) produced the best morphological structure of rCF.

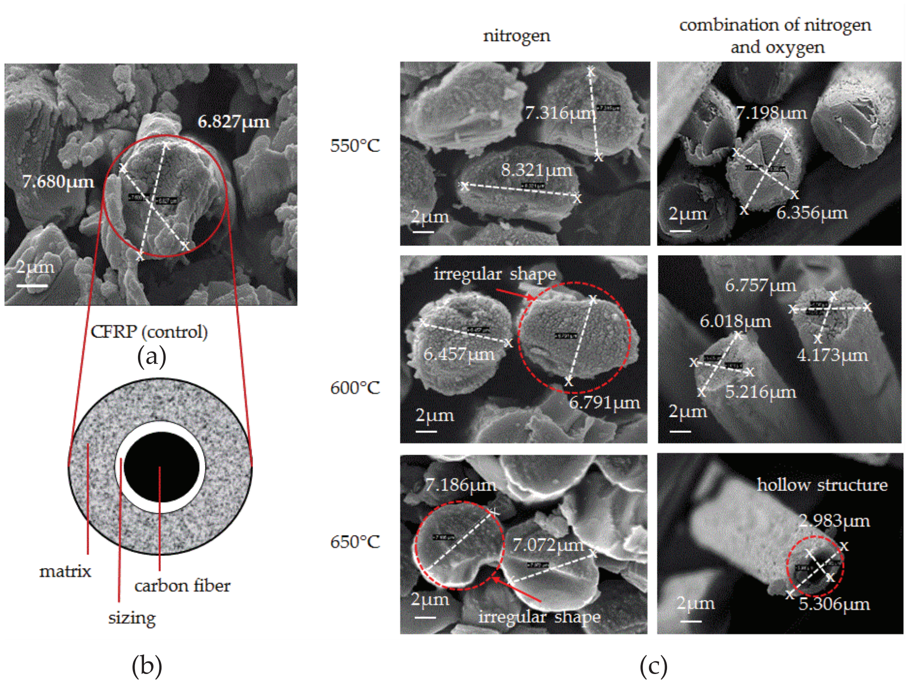


Figure 2: Cross sectional analysis of (a) CFRP, (b) schematic diagram of CFRP and (c) rCF after thermal decomposition at different atmosphere and final heating temperature

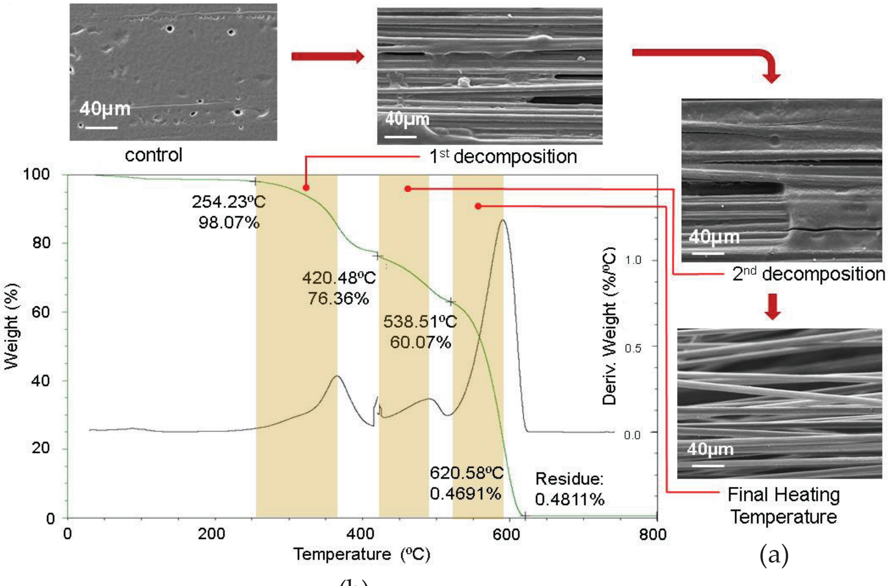
It can be inferred that pyrolysis using single atmosphere of nitrogen is not effective, since a complete separation of CF from their complex matrix is not effective, since a complete separation of CF from their complex matrix is not achieved. Oxygen does not influence the decomposition of the resin up to 400⁰C, since it burns out everything to carbonaceous residue as reported by Tranchard et al. [8]. However, the oxygen plays a role to complete the decomposition at higher temperature in nitrogen-based decomposition of CFRP. Meyer et al. [14] found similar results of rCF in combination atmosphere of nitrogen followed by oxygen conditions. They found the fibres maintain their structure without resin residue on the surface.

High residue at higher final heating temperature (600⁰C to 650⁰C) indicates unsuccessful separation of rCF due to pyrolytic carbon creation [13]. Indeed the surface degradation observed for oxygen atmosphere at higher temperature (600⁰C to 650⁰C) is suggested to be correlated with decomposition of CF. Thus, low final heating temperature (550⁰C) resulted in more efficient epoxy resin removal with rCF structure reservation than higher final heating temperature.

3.2 Mechanism of Thermal Decomposition

As far as the best final heating temperature of 550°C is concerned, TGA was performed to understand further the thermal decomposition behavior. Figure 3(a) shows morphological examination from SEM coupled with TGA of CFRP decomposition (Figure 3(b)) when combination of nitrogen atmosphere at the early stage (250 to 420^{0}C) followed by oxygen atmosphere at high temperature (420 to 540^{0}C) is applied. Apparently, there are three significance stages of decomposition mechanism. Compared to CFRP (control), first stage of decomposition in nitrogen atmosphere approximately at 300^{0}C reveals the degradation of epoxy resin that covered the CF. CF at this stage is still tightly bonded to each other due to incomplete removal of epoxy resin.

Next, second stage of thermal decomposition at temperature range 420^{0}C and 500^{0}C produced clearer and looser bundle of rCF, but still with sizing and epoxy resin covered on their surfaces. Finally, at approximately 540^{0}C, clean and smooth individual rCF is observed. Here, it can be inferred that temperature 540^{0}C in oxidative atmosphere is recognized as the real final heating temperature to sustain solid rCF and removed almost 100% of epoxy resin and sizing.



(b) (a)

Figure 3: Thermal decomposition mechanism of CFRP: (a) step by step of SEM micrograph of CRFP thermal decomposition and (b) TGA of CFRP thermal decomposition

During the first stage of decomposition, the nitrogen atmosphere is important factor that contribute to the transform of matrix into smaller molecules. However, some pyrolytic carbon (residue) bonded to the rCF surface are still remains. This rCF is further heated in the nitrogen atmosphere to remove the epoxy resin and sizing completely. When oxygen is purge after 2nd decomposition stage, at temperature 420^0C, the complete burning of pyrolytic carbon take place until final heating temperature 540^0C.

Meyer et al. [14] found that in the synthetic air environment, complete removal of all the matrix can be achieved within the temperature range from 580 to 600^0C. In agreement, Liu et al. [15] in their review of optimization techniques used in the composite recycling area also suggested complete elimination of the complex matrix of CFRP using thermal decomposition at the temperature up to 600^0C. However, based on the results presented, this study suggests that further heating above 540^0C will lead to the third decomposition stage of rCF and will cause degradation of their surfaces.

3.3 Raman Spectroscopy Analysis

Raman spectra were used for the spectroscopic characterization of carbon fibers. Figure 4 illustrates Raman spectroscopy of rCF produced from pyrolysis at final heating temperature of 540°C. The main features in the Raman spectra of rCF shown in Figure 4 are known as G and D bands, which are centered at around 1590 and 1380 cm^{-1}, respectively. The G-band is attributed to the in-plane vibrations of sp^2-bonded crystalline carbon and has been observed in single crystal graphite, while D-band, is assigned to the in-plane vibrations of sp^2-bonded carbon with structural imperfections [16-17]. However, two significant Raman peaks also appear at 960 and 1041cm^{-1}.

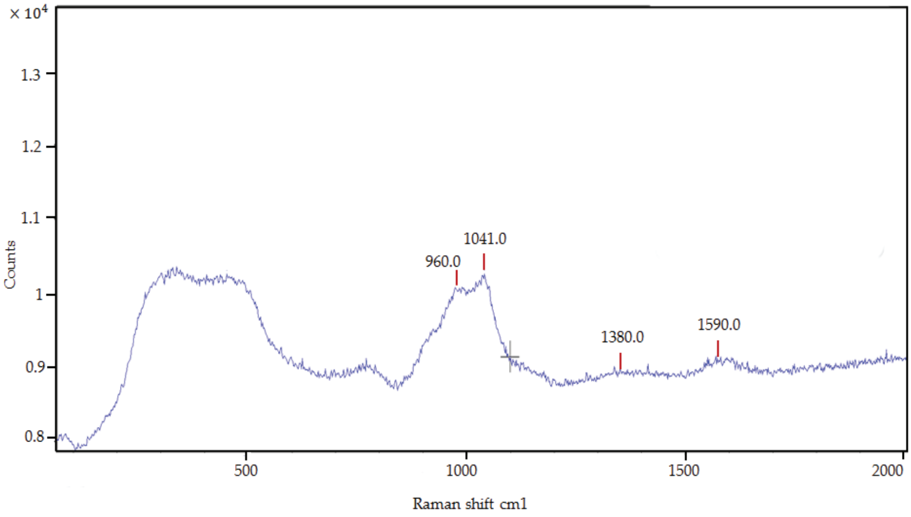


Figure 4: Raman spectroscopy of rCF produced at final heating temperature 540°C

The broad peak of G-band might be associated with rCF that was still hindered and surrounded by residues after pyrolysis. It was supported by significant peak at 960 and 1041cm^{-1} Raman spectra. These peaks could be attributed to left resin which is not completely eliminated during pyrolysis. Raman peaks in the range of 800-1600 cm^{-1} mainly related to the carbon backbone have been previously associated with crystalline structure of epoxide ring [18] and polyamides [19]. This result suggests for further purification on the rCF surfaces. Purification might be done via simple chemical process.

4.0 CONCLUSION

Recycling CF from CFRP via pyrolysis is proposed to be cheap and effective methods. Via this technique, efficient separation of CF from their matrix while maintaining their structure could be achieved at final heating temperature of 540^{0}C and combination atmosphere of inert nitrogen atmosphere at the early stage followed by oxygen at the end of burning process. Further morphological and structural analysis done by SEM and Raman spectroscopy supported those findings proven that pyrolysis with careful examination of final heating temperature and atmosphere could produce clean surfaces and preserve uniform spherical shape of rCF to be applied for secondary industrial application. However further purification process is needed to completely produce clean rCF.

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