# Oxidation of Reclaimed Carbon Fiber Surfaces for The Improvement of Fiber/Composite Adhesion

Norazlina Mohamad Yatim[1*], Zurina Shamsudin[1], Azizah Shaaban[1], Nurhernida Abdullah Sani[1], Ridhwan Jumaidin[2], Emy Aqila Shariff[3]

[1] Centre of Smart System and Innovative Design, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[2] Fakulti Teknologi Kejuruteraan Mekanikal dan Pembuatan, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[3] Composites Technology Research Malaysia, Jalan Merdeka 33, Taman Merdeka, 75350 Batu Berendam, Melaka, Malaysia.

## Abstract

The recovery of carbon fiber (CF) from carbon fiber reinforced composites (CFRP) waste provide valuable reinforcement material for secondary structural application. Although surface modification of reclaimed-CF can improve its interfacial compatibility with composites, it may affect its strength and capability as a reinforcing material. This paper investigates the influence of different reflux time (10 – 50 min) on the oxidation of reclaimed-CF surfaces using nitric acid. The reclaimed-CF was recovered using a combination of nitrogen and oxygen atmospheres during pyrolysis at low final heating temperature (540°C). The surface chemical composition and morphology of the reclaimed-CF were investigated via FT-IR and SEM respectively. Microscopy analysis shows low nitric acid oxidation time (20 min) effectively removed residues of resin prior pyrolysis and produced a clean reclaimed-CF surface. Further oxidation activated the reclaimed-CF by the creation of more acidic functional groups on their surfaces. The acidic capacities increase with oxidation time without damaged the tubular reclaimed-CF structure. Overall, the optimized nitric acid treatment produced cleaner reclaimed-CF surfaces and more active sites for better interfacial compatibility between reclaimed-CF and composite matrix.

**Keywords:** Recovery, carbon fiber, waste, pyrolysis, acidic treatment.

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*Corresponding author: Norazlina Mohamad Yatim ; email: norazlina.yatim@utem.edu.my

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## Introduction

The global demand for CF is significantly growing at a rate of 9-12% until 2022 1]. Carbon fibers (CF) are the perfect reinforcement material for polymer composites in high-end application industries like aerospace due to their advantages of high strength and low weight. This CFRP complex design mainly composed of an epoxy resin, virgin CF and thermoplastic polymer. Currently, 'Carbon Prepreg' in the aerospace composite industry, constitute of CF which pre-impregnated with resin 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 and left the excess as wastage. However, their amount is continuously increased every year also with other forms of waste like production cut-offs and end-of-life components [2]. Recognizing a significant amount of wastage generated, recycling CFRP is essential to recover this reclaimed-CF for application in new composites as secondary reinforcement materials for the sake of the environment through the reduction of waste at the landfill.

Thermal decomposition such as pyrolysis was a promising and lower cost method to recover CF from complex CFRP composite [3]. However, the heating profile is different from one system to another as it depends on the chemical nature of their components [4–6]. Dealing with high-value products such as CF, other recycling methods like mechanical technique which results in a powdered form of carbon will alter the individual fiber structure after the composites are crushed. While high-cost chemical recycling removed the matrix from the CF using different harmful acidic solvents. Optimized and improved low-cost pyrolysis utilized heat energy to recover the CF, make it become the most guaranteed method for recycling CFRP [7]. However, pyrolysis might produce left residues on the reclaimed-CF surfaces which need further surface treatment to produce eliminate resin residues.

Thus, further post-treatment following pyrolysis is essential to improve the quality of reclaimed-CF and completely clean the reclaimed-CF surface. In a former study different parameters during pyrolysis such as final heating temperature and atmosphere were investigated and optimized. The reclaimed-CF was able to recover by pyrolysis technique at low final heating temperature (540°C) in combination atmosphere of nitrogen at the early temperature followed by oxygen atmosphere at the higher temperature. However, the reclaimed-CF without post surface treatment and impregnated in composites will result in low interlaminar shear strength (ILSS) due to weak adhesion and poor bonding between the fiber and matrix [8]. Nitric acid oxidation surface treatment was reported to enhance the surface area and surface acidic functional groups of reclaimed-CF [9] and lead to enhancement of reclaimed CF/resin matrix bonding. In this study, the effect of nitric acid oxidation treatment at different oxidation times on morphological properties of reclaimed-CF will be investigated to activate its surfaces for reclaimed-CF/composite adhesion improvement.

## Materials and Methods

### *Materials*

A roll of carbon fibre 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. Nitric acid (69%), from MERCK was used at analytical grade.

### *Pyrolysis Process*

The 10 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 a tube furnace of pyrolysis machine. The tube was vacuum first to obtain an absence of oxygen for the burning process. Inert gas of nitrogen at the early temperature (250 - 420°C) and oxygen at a higher temperature (420 - 540°C) was used as a controlled environment at 5cc/mm3 gas pressure. The furnace machine was then being programmed with the requirement final heating temperature (540°C).

### *Surface Treatment of Reclaimed Carbon Fiber*

The reclaimed-CF was reflux in nitric acid (100°C, 20rpm) at a different time (10, 20, 30, 40 and 50 minutes). Then, the samples were vacuum filtered and wash 10 times with distilled water until neutral before dried in an oven (120°C) for 2 hours.

### *Morphological Analysis*

Morphological behavior of CFRP and reclaimed-CF were analyzed using scanning electron microscopy (SEM). Surface functional group elimination of CFRP and reclaimed-CF were investigated using FT-IR spectroscopy (JASCO FT-IR, 6100), recorded in a range of 400 to 4000cm-1 with a resolution factor of 4cm-1 via ATR method.

## Results and Discussions

### *Chemical Analysis of Acidic treated reclaimed-CF*

FT-IR analysis aims to characterize the modification occurred on the reclaimed-CF surfaces after acidic treatment. Figure 1 shows the main functional groups produced during the oxidation process. Different reflux time for nitric acid treatment was selected and compared to reclaimed-CF without treatment as control. Control shows FT-IR spectra of almost flat without any significant functional groups. While all treated reclaimed-CF (10 - 50 minutes) that reflux with nitric acid, reveal O-H functional group of epoxy at ~3700 $cm^{-1}$ and C≡N stretching of acrylonitrile unit in the polymer chain at 2240 $cm^{-1}$ [10]. The weak absorption at 1626 $cm^{-1}$ may be attributed to C=C ($\nu_{C=C}$) [11]. Another important functional group observed are C=O (~1600 $cm^{-1}$) and C=C (~1550 $cm^{-1}$). Tiwari et al. [12] were also observed FT-IR spectra at wavenumber range of 1650-1710cm-$^{1}$, corresponding to carboxyl and carbonyl groups for oxidation treated CF. Hence, via this oxidation method, acidic functional groups were observed to produce and activate the reclaimed-CF surfaces.

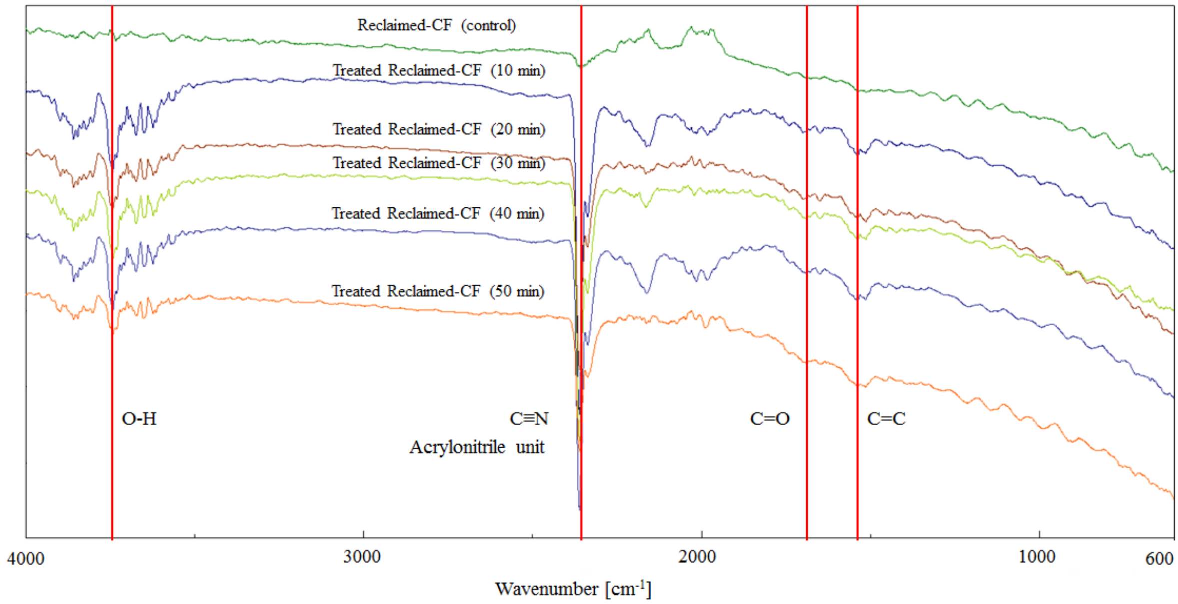


**Figure 1: FT-IR analysis of treated reclaimed-CF as compared to reclaimed-CF (control).**

FT-IR analysis reveals complete elimination of epoxy matrix and left carbon FT-IR pattern attributed to solid reclaimed-CF. The occurance of important functional groups on the treated reclaimed-CF surfaces shows that oxidation has activated their surfaces with acidic functional groups. The effectiveness of the treatment in improving the reclaimed-CF surfaces depends on the oxidation treatment time. Earlier research work by Wu et al. [13] concluded that acidic capacities of CF increased almost linearly with the oxidation time. Tran et al. [14] in their research work to investigate the impact of oxidation modification on CF reported that with increasing severity of oxidation, the surface oxygen and nitrogen content increased. This treatment led to an increase in overall surface energy of the CF. Existence of acidic functional groups on reclaimed-CF surface will increase its chemical reactivity and compatability with matrix. These active groups were accountable for adhesion enhancement with matrix [15]. Here, activation of reclaimed-CF surfaces was achieved by oxidation via reflux with concentrated nitric acid at various oxidation time (10-50 min).

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***Morphological Analysis of Acidic treated reclaimed-CF***

***Reclaimed-CF production by pyrolysis***

Figure 2 shows the micrograph of untreated reclaimed-CF produced via pyrolysis. Generally, pyrolysis maintains the tubular structure of CF with clean and smooth surfaces and are separated from each other (Figure 2A). However, further investigation under higher SEM magnification, a few tiny fractured residues in nano-sized of resin were found left on the reclaimed-CF surfaces. The fractured residues scattered along the reclaimed-CF surfaces. A cross sectional analysis of SEM (Figure 2B) shows clearer individual reclaimed-CF, separated from each other. The reclaimed-CF after the epoxy resin elimination through pyrolysis shown consistency in size with commercial CF, mainly in range of 6 to 9 um in diameter [16]. Reclaimed-CF end-surfaces were observed to have a unified spherical shape.

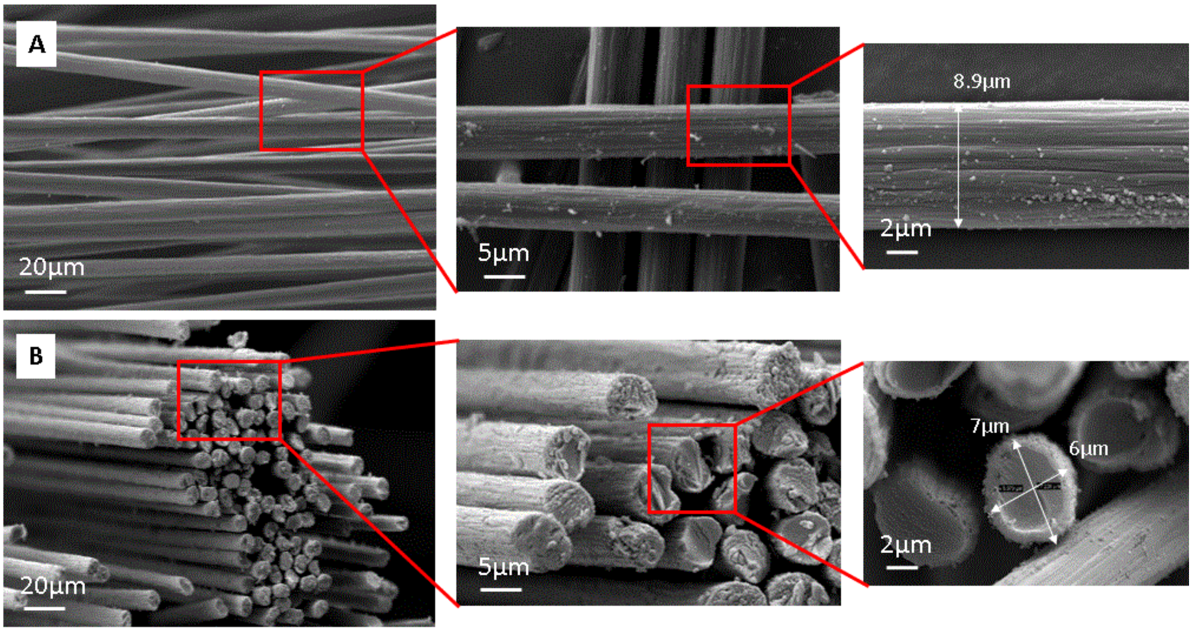


**Figure 2: SEM micrograph of untreated reclaimed-CF produced via pyrolysis**.

Through thermal decomposition of pyrolysis, the polymeric matrix is broken down in inert atmosphere and by-products formed consist of organic materials in gas and/or liquid form followed by complete burning of pyrolytic carbon in oxygen atmosphere at high heating temperature, leaving the reclaimed-CF in solid form. Meyer et al.[17] reported earlier that in oxidative atmosphere, the CF are still covered by matrix residues at 500°C and completely removed at 600°C. However, the final temperature of 540°C applied in this study with combination atmosphere of nitrogen and oxygen manage to produce clean reclaimed-CF without structural damage. Further heating might damage the tubular structure and reclaimed-CF surfaces. Particular heating profile consist of final temperature and atmosphere are the key parameters that must be carefully adjusted according to specific type of CFRP waste because they reflects a significant effects in the morphology of reclaimed-CF produced via pyrolysis. However, further treatment to eliminate completely the left residues is needed.

### *Oxidation surface treatment produced clean reclaimed-CF*

The effect of oxidation treatment on reclaimed-CF surfaces is illustrated in Figure 3. As compared with control (Figure 2) the reclaimed-CF was still covered with nano-sized fractured residues of resin which not completely eliminated via pyrolysis. Prior to oxidation surface treatment for the period of 10 minutes reflux in nitric acid (Figure 3A), the reclaimed-CF surface become cleaner from fractured residues of unwanted CFRP waste resin. The roughness and cleanliness of reclaimed-CF surface increased with an increase in oxidation time up to 20 minutes (Figure 2B). 20 minutes reflux time produced the best morphological structure of reclaimed-CF, while further oxidation 30 minutes reflux time with nitric acid (Figure 3C) created grooves and black etch pits on reclaimed-CF surfaces.

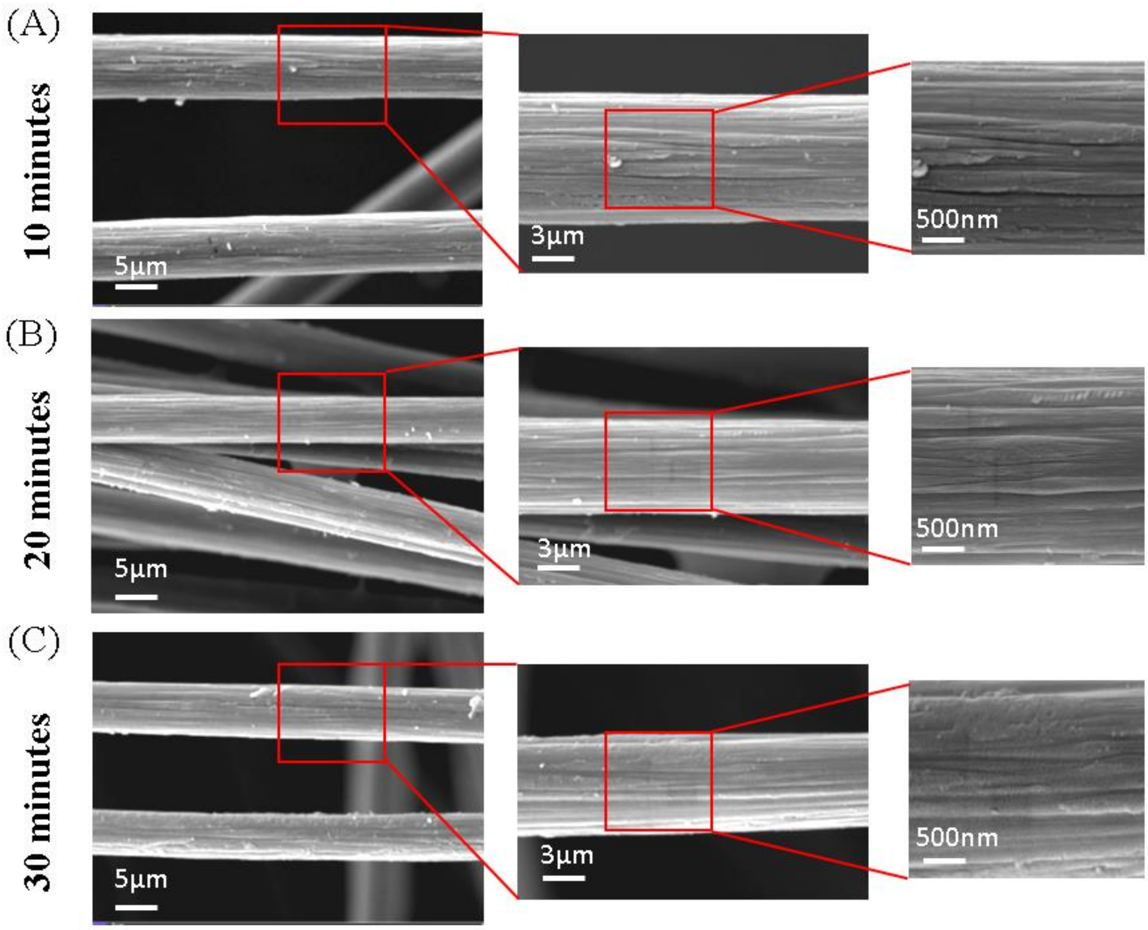


**Figure 3: Effect of oxidation surface treatment on the morphology of reclaimed-CF.**

Thus, oxidation treatment of 20 minutes was found capable enough to clean and completely eliminate left residues on reclaimed-CF surfaces. While further treatment until 30 minutes reflux time increase reclaimed-CF surface roughness which corresponding to increment in surface area. The surface roughness increased due to grooves formation on the reclaimed-CF surfaces by removing the amorphous carbon during the nitric acid treatments leads to increase of binding sites on material surface [9]. Tiwari et al. [12] modified their CF by boiling in nitric acid from 15 to 180 minutes also observed that with increasing treatment time, roughness of fiber surface increased together with production of ether, carboxyl and carbonyl groups on CF surfaces. Hence, this method was efficient as complimentary treatment for pyrolysis to produce clean reclaimed-CF. However, increasing treatment time might be needed to provide more active sites for the reclaimed-CF.

***Oxidation treatment activated reclaimed-CF surfaces***

Figure 4 illustrates morphological changes of reclaimed-CF surface prior oxidation treatment. Apparently, with increasing treatment time, roughness and grooves structure of reclaimed-CF surface increased, while maintaining its tubular structure. However, grooves structure on reclaimed-CF surfaces become more apparent as treatment time increase until 50 minutes. The whole reclaimed-CF tubular structure seems to be covered with a surface layer of acidic functional groups active sites as result from oxidation treatment.

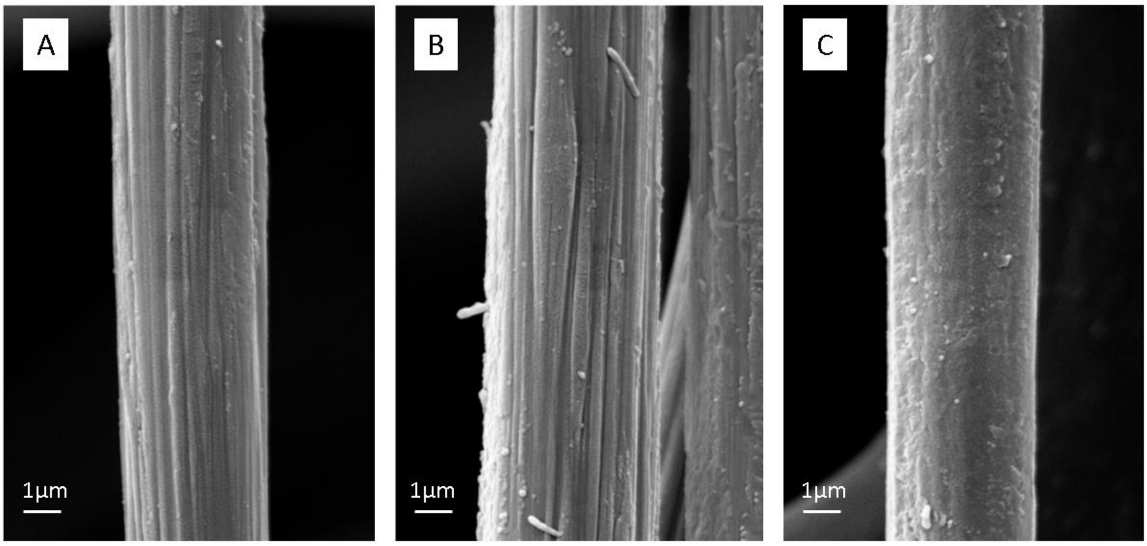


**Figure 4: Effect of further oxidation surfaca treatment on the morphology of reclaimed-CF (A) 30 minutes, (B) 40 minutes (C) 50 minutes**

As the treatment time increases to 50 minutes, there appeared more closely spaced deep grooves on the surface of treated reclaimed-CF, which improved the surface roughness subsequently rises the surface area and provides more active sites on fiber surface for better mechanical interlocking between carbon fiber and matrix [12]. Therefore, chances to perform a strong bonding between reclaimed-CF and the matrix is increased as more active functional groups introduced on the reclaimed-CF surfaces. Thus the load stress applied could be transmitted effectively from the matrix to fibers, for the reclaimed-CF successfully carry the load.

## Conclusion

Oxidation surface treatment is an essential complementary for pyrolysis recycling methods to recover CF from CFRP industrial waste. Oxidation at lower reflux time effectively clean the reclaimed-CF surfaces and completely eliminate resin residues. Further oxidation treatment improve surface area and provides more active sites for the reclaimed-CF without damaging the tubular structure to enhance its adhesion with various matrices via strong bonding. Hence, reclaimed-CF could act as good reinforcement material in composite by successfully carry the load stress transmitted.

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## Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

## Disclosure of conflict of interest

The authors have no disclosures to declare.

## Compliance with ethical standards

The work is compliant with ethical standards.

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