RECLAIMED CARBON FIBRES TREATED BY PYROLYSIS OF NITROGEN AND INERT GAS

Zurina Shamsudin[1*], Norazlina Mohamad Yatim[1], Azizah Shaaban[1], Zaleha Mustafa[1], Toibah Abd Rahman[1], Muhamad Mirza Hairudin[1], Jamari Abdul Ghafar[2]

[1]Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka , Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Composites Technology Research Malaysia, Jalan Merdeka 33, Taman Merdeka, 75350 Batu Berendam, Melaka, Malaysia;

Email: zurina.shamsudin@utem.edu.my

ABSTRACT: *Reclaimed carbon fiber (rCF) provides a high possibility to be reused as reinforcement for new composite aiming secondary structural applications. This study's intention is to evaluate the strength and modulus of rCF produced via pyrolysis on waste uncured prepreg using a quartz tube furnace. The optimization of the pyrolysis parameters (temperature and dwelling time) is done by using the Taguchi design of the experiment. Inert gas of nitrogen was used as the control environment. The single fiber testing was carried out to evaluate the mechanical properties of the rCF including strength and modulus properties before being analyzed via the Weibull approach. Through surface morphology observation, the resin on rCF surfaces has been removed efficiently at a pyrolysis temperature of 550°C and 2 hours of dwelling time with the rCF sizes retained at 6µm in diameter average. Single fiber testing results showed the average ultimate tensile strength of rCF is 11.3 MPa and the average modulus of the rCF is 0.127GPa. The Weibull distribution demonstrated that the pyrolysis process be able to reclaim waste carbon fibres at minimum cost and retain their good mechanical properties.*

KEYWORDS: reclaimed carbon fibre, single fibre testing, pyrolysis

1.0 INTRODUCTION

Carbon fibre reinforcement polymer (CFRP**)** has been widely used in high-end industries as a structural material due to its low weight and high strength advantages. As reported by Kuhnel and Kraus [1], the CFRP market is expected to reach 191000 tons of demand by 2022. The dramatic increase in carbon fiber demand and application lead to the rise of generated waste either as an off-cut type of material or as an end-of-life composite product. However, most of the carbon fiber-reinforced polymer waste goes to landfill whose area is limited and the cost to dispose of is high [2]. Hence, it appears to be critical to develop suitable composite recycling technology that could offer interesting environmental and economic properties.

Since it is expensive to produce CFRP due to the very high energy cost needed to convert the polymer base into carbon fiber, the development of advanced recycling techniques for reclaiming carbon fiber is totally required [3]. One of the most popular recycling processes is pyrolysis [4]. Pyrolysis is the thermal decomposition of organic molecules in an inert atmosphere [5]. It has been the most studied thermal process [6]. The efficiency of such treatment was high, varying from 80% to 99% of eliminated resin, depending on the matrix nature and considered variables. The challenge to overcome is rCF tensile strength degradation due to the presence of char on the fiber surface as a result of the inefficient pyrolysis process. However, pyrolysis is well known as a cost-efficient technology well suited to the relatively undeveloped composites recycling market, thus the most convenient way to reclaim carbon fiber from CFRP. The parameter concerned for lab-scale pyrolysis process control includes final temperature, type of gas, and pressure. As far as environmental impact is concerned, this type of thermal process is conducted at low temperatures with an optimized process to increase reclaimed process performance through a controlled treatment process.

Previously, Pickering et al. [7] used pyrolysis in their studies for industry and commercialization scale. However, in order to produce high-quality reclaimed carbon fiber (rCF) owing to the current lack of information about the pyrolysis process of lab-scale production mainly for high-performance carbon fibre composite. A comparative study on the performance of rCF should be extended in order to investigate the effect of process pyrolysis and the relationship between the morphology of the rCF. Therefore, an improvement and optimized pyrolysis process from Pickering et al. [7] research work with nitrogen as control environment are present. Improvement in tensile strength and modulus of rCF can be achieved via efficient resin removal through an optimized pyrolysis process considering single fiber tensile test (SFTT) as proposed mechanical characterization. An optimal pyrolysis process is able to avoid damage to the fibers during the resin removal and get a perfect alignment of the rCF. The tensile strength determination then will provide valuable information on whether rCF production is able to reach more than 70% of commercial carbon fiber mechanical properties at a minimum cost of production. This work intends to design, and reclaim the carbon fibers, tested in mechanical tests and finally recorded the basic data for the lab-scale pyrolysis process.

2.0 MATERIALS AND 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. was used for this research. Type of CFRP are not reported due to a confidential agreement. The plain prepreg made of epoxy resin reinforced with carbon fibers (60% carbon fibers [by volume] and 40% complex epoxy resin).

2.2 Pyrolysis process

The 400 g of CFRP was cleaned with distilled water before being cut into a small size (100mm x 20mm) to be fitted in the ceramic crucible and placed in the tube furnace of the pyrolysis machine. Inert gas of nitrogen was used as the control environment at 5cc/mm^3 gas pressure. The tube was vacuumed first to obtain an absence of oxygen for the burning process. The furnace machine was then programmed with the required temperature and dwelling time with heating rate of 10°C/min.

2.3 Optimization of pyrolysis parameters by Taguchi method

Design of Experiment (DOE) using 3 level Taguchi method with main effects as design model via standard Orthogonal Arrays (OA) for forming a matrix of experiments attempts to extract the effect of factors as individual and interaction between them. Taguchi's design of the experiment for completing the pyrolysis process is shown in Table 1, involved two factors selected which were final heating temperature (550- 650°C) and dwelling time (1-3 hours) with nitrogen as the control environment with a gas flow rate of 200cc/min. The range of final heating temperature and dwelling time were selected based on the research statement of the reclaimed carbon fibre treated by pyrolysis that affectfiber the mechanical and physical properties [4]. Taguchi's method was chosen to help on the designing the experimental sequence of the parameters with CFRP as control specimen.

Table 1: Taguchi's design of experiment.

Run	Factor 1 A:Final Temperature (°C)	Factor 2 B:Dwelling Time (hour)
1	550	2
2	650	1
3	550	1
4	650	2
5	600	1
6	650	3
7	600	3
8	600	2
9	550	3

2.4 Mechanical property measurement

The strength of a single rCF is tested by single fibre testing. The rCF were soaked in the ethanol solution of 95% concentrated for a day followed by being soak in acidic solution and been boiled for a while. The rCF were cut into 40mm in length, *l* (Figure 1) as to fit the card frame that was cut with a dimension of 65mm x 20mm and a gage length of 25mm for getting it fit with a gage length 25mm. Then, the single fiber was carefully placed onto the Shimadzu EZ-LX Universal Testing Machine, followed ASTM C1157-03 standard of sample preparation. The best 50 sample of rCF were collected as it passed through the weighing exchanges and the microstructure observation. The test was conducted at a constant rate of displacement of 0.2mm/min with load cell was rated to 10N. Statistical analysis of Weibull distribution was conducted. The strength was evaluated by using the formula as below:

$$Area, A\ (mm^2) = \pi r^2 (r + h)$$

Eq. 1.1

$$\boldsymbol{Strength, \sigma\ (Nmm^{-2})/(Pa) = \frac{Force\ (N)}{Area\ (mm^2)}}$$

Eq. 1.2

$$Strain, \delta = \frac{Displacement\ (mm)}{Gage\ length\ (mm)}$$

Eq. 1.3

$$Modulus, \in = \frac{Stress, \sigma}{Strain, \delta}$$

Eq. 1.4

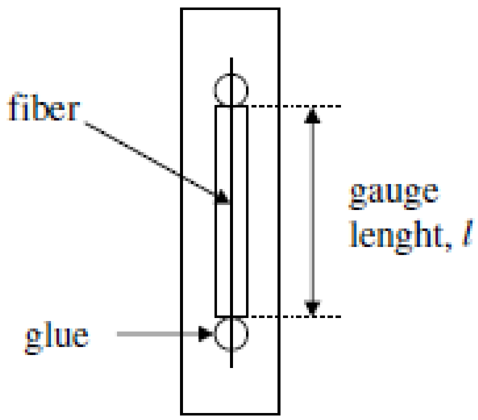

Figure 1: The schematic of sample preparing single fibre test and the Shimadzu EZ-LX Universal Testing Machine (Japan)

2.5 **Statistical distribution of fiber strength**

Weibull analysis was used for the fracture statistic of rCF. For a single gauge length and uniform uniaxial tensile stresses, the Weibull equation of failure probability is given by:

$$P = 1 - exp\left[-\left(\frac{V}{V_0}\right)\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right]$$

Eq. 2

Where V is the stressed volume and V_0 a reference volume, $\varepsilon_0 = \frac{\sigma_0}{E_f}$, σ_0 being the scale factor, E_f the Young modulus of a fibre, and *m* the Weibull modulus. As a common approach, a Weibull diagram is usually constructed by using empirical estimators of failure probability. Then, the statistical parameters are obtained by fitting (2) to the Weibull plot. The Weibull distribution parameters from single fibre testing were determined by the weakest link theory method (WLT).

2.6 **Surface morphological analysis**

The surface morphology of rCF is observed by using scanning electron microscopy (SEM), brand ZEISS EVO 50. Prior to the scanning, the rCF were coated in gold (80% gold and 20% palladium) for conductivity improvement and charging effect reduction via Quorum sputter coater SC 7620.

3.0 RESULTS AND DISCUSSION

3.1 Optimization via Taguchi design of experiment

The total of 9 set of experiment structured via 3 levels Taguchi method with main effects as design model and weight difference as Taguchi's response is shown in Table 2. In the present reaction system two operating parameters (final heating temperature and dwelling time), each at three levels, are selected to evaluate weight difference after pyrolysis. Generally, the weight of the CFRP as corresponding respond was generally reduced prior to pyrolysis for all samples, which then give positive value of weight difference. The weight difference varied from 1.03 to 2.36 as final heating temperature varied from 550 to 650°C. The weight difference values also increasing as dwelling time increase from 1 to 3 hour.

Table 2 Response values of weight difference for Taguchi's Method Design of Experiment.

	Factor 1	Factor 2	Response 1
Run	A:Final Temperature	B:Dwelling Time	Weight Difference
	(°C)	hour	g
1	550	2	1.35
2	650	1	1.03
3	550	1	1.13
4	650	2	1.28
5	600	1	1.2
6	650	3	1.53
7	600	3	1.38
8	600	2	1.29
9	550	3	2.36

Referring to Table 1, the weight reduction after pyrolysis showed that some of the polymers and resin embedded with CFRP were removed during pyrolysis process. The variation in final heating temperature selected are significant in removing the resin to reclaim the carbon fibre. The weight difference values are increasing as dwelling time increase due to successful acid treatment in further remove the resin in CFRP to produce better rCF. Physically, after pyrolysis the samples were in fluffy form and dull in color as there is no longer any size holding the fibres bundles together compared to samples before pyrolysis.

3.1.1 ANOVA for selected factorial model

ANOVA for selected Taguchi factorial model with weight difference as selected response is listed in Table 3.

The Model F-value of 2.39 implies the model is not significant relative to the noise. There is a 20.96% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Hence, model reduction may improve the model selected when the model term is insignificant.

Table 3 ANOVA for weight difference as selected response.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	0.8584	4	0.2146	2.39	0.2096
A-Final Temperature	0.2158	2	0.1079	1.20	0.3901
B-Dwelling Time	0.6427	2	0.3213	3.58	0.1284
Residual	0.3590	4	0.0897		
Cor Total	1.22	8			

3.1.2 Fit Statistics

The model fit statistics is shown in Table 4. A negative predicted R^2 implies that the overall mean may be a better predictor of your response than the current model. In some cases, a higher-order model may also predict better. However, this model was chosen to discuss both final temperature and dwelling time as factors for the pyrolysis parameters**.** Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable, and a ratio of 4.344 indicates an adequate signal. Hence, this model can be used to navigate the design space.

Table 4 Fit statistics for selected factorial model

Fit statistics	value
Std. Dev.	0.2996
Mean	1.39
C.V. %	21.48
R^2	0.7051
Adjusted R^2	0.4103
Predicted R^2	-0.4928
Adeq Precision	4.3441

3.1.3 Solution from optimization process of pyrolysis process

The solution given from optimization of pyrolysis process parameter via Taguchi method is shown in Figure 2. The highest desirability (0.711) and 1.97556 predicted weight differences were getting from 550°C of final heating temperature and 3 hour dwelling time. Hence, this solution is selected for further surface morphology analysis.

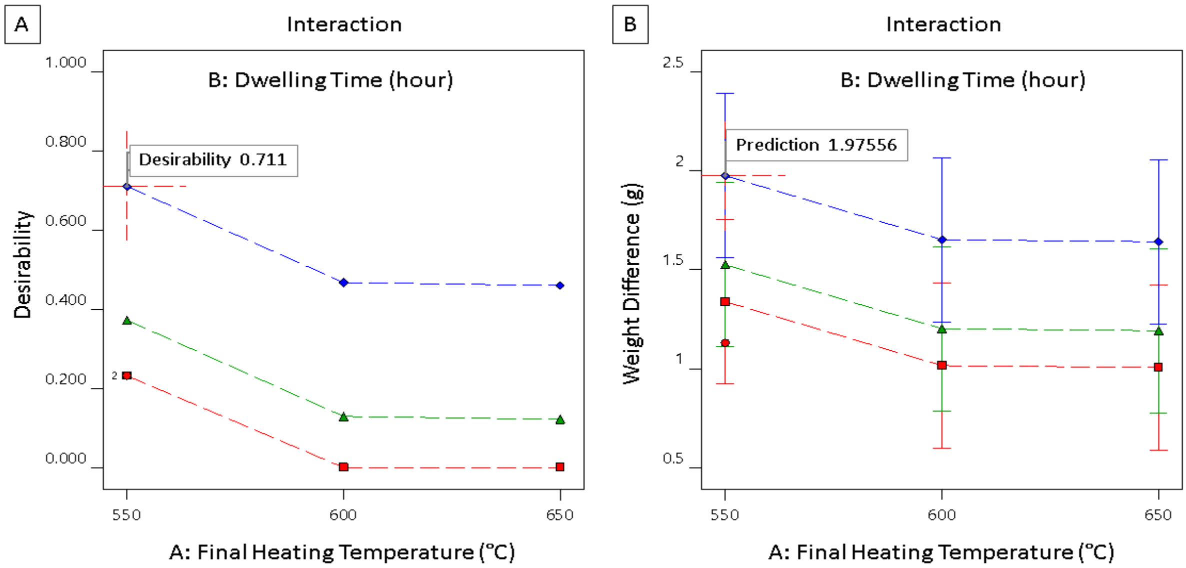

Figure 2: Solution prior interaction effects of final heating temperature and dwelling time.

3.2 Strength of reclaimed carbon fiber

Table 5 shows the diameter, average percent of stress, strain, and modulus of the rCF. All diameter of 10 samples were retain around 6 to 7 micrometres. Single fiber testing result showed the average ultimate tensile strength of rCF is 11.2805MPa and average modulus of the rCF is 0.127GPa compared to control

.Table 5 Reclaimed carbon fibres mechanical properties.

Sample	Diameter (µm)	Stress %	Strain %	Modulus (GPa)
1	6.4	0.44	7.83	0.05
2	6.4	0.73	4.99	0.17
3	5.9	0.48	3.46	0.14
4	6.2	0.58	4.04	0.14
5	6.8	0.46	4.41	0.10
6	6.7	0.74	6.41	0.12
7	6.3	1.13	8.26	0.14
8	6.4	0.47	3.86	0.12
9	6.4	2.21	15.03	0.15
10	6.5	0.88	6.09	0.14

The average tensile strength and modulus of rCF evaluated from single fibre tests that were selected free from deformation and visible inconsistency to the naked eyes were 11.3 MPa and 0.127GPa, respectively. The average tensile strength of rCF was observe to decrease previous work by Pickering [7]. This implying that possible the fibre treated flaws caused the stress concentration where were directly related to during sample preparation handling. The total of surface damage on the carbon fibres might be expected due to increase arising from heat. This may be attributed to the scattering in strength as these defects are created during high temperature of pyrolysis which degraded the carbon fibres strength [8].

3.3 Weibull Analysis

The Weibull distribution parameters from single fibre testing were determined by the weakest link theory method (WLT) and were evaluated under constant gauge length. The Weibull parameter `m', was referred as a flaw regularity distribution factor [9]. A summary of the Weibull parameter values calculated were listed in Table 6 using Equation [2]. Single fiber testing result showed the Weibull moduli of rCF is 0.2459 and the characteristic strength is 0.127GPa which lower from the work by Pimenta and Pinho [10].

Table 6 Weibull charactiristic

Sample	Gauge length, L (mm)	Weibull modulus (m)	Characteristic strength, σ_0 (GPa)	R^2
rCF	25	0.2459	9.928	0.0379

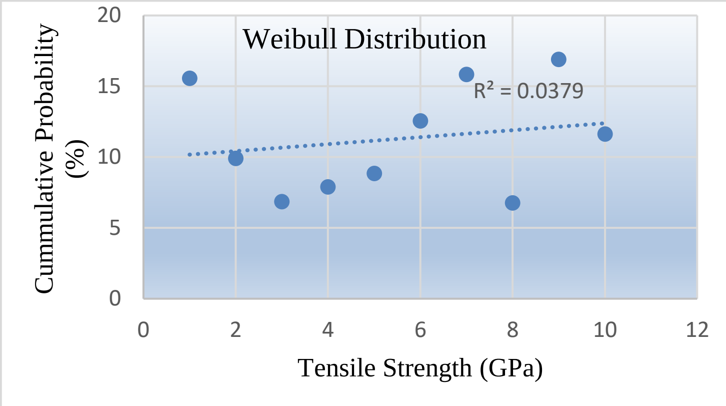

Figure 3: Weibull Distribution

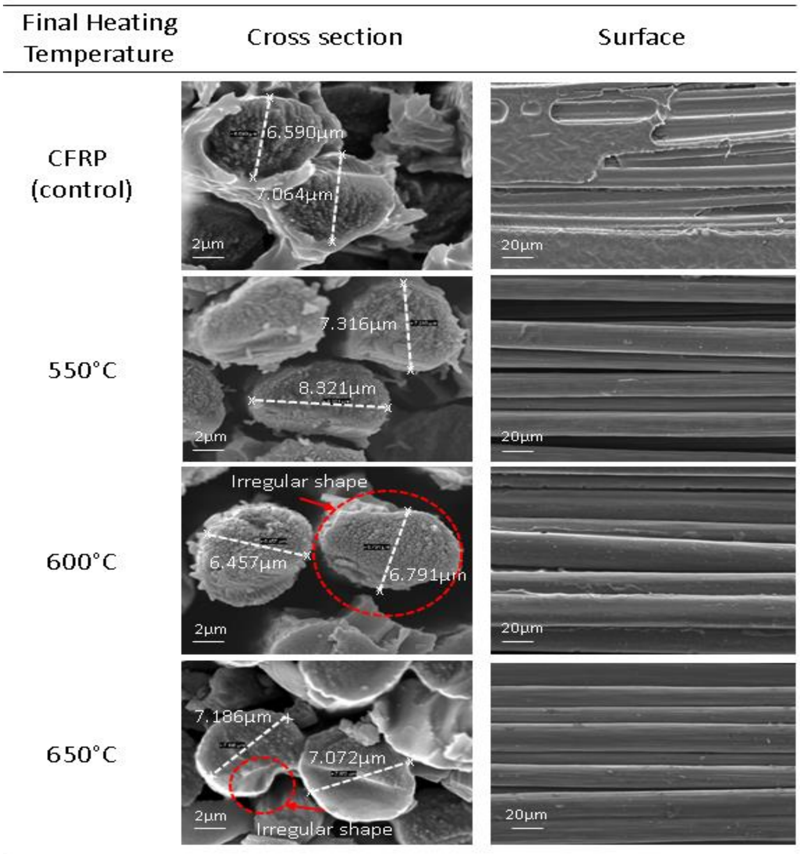

Figure 4: Surface morphology analysis of rCF as compared to CFRP

The lower value of Weibull modulus and characteristic is likely caused to be caused by the introduction of the flaws during the handling and treatment, mainly during the pyrolysis. This can be supported from the Figure 3 where the diameter values recorded via SEM shows inconsistent diameter and the shape of the fibre where non-uniform fibres after pyrolysis process. These maybe the source of scatter in strength data as represent in Figure 4 which contributed the R^2 coefficient far from 1 [11], indicating a poor degree of linearity.

It can be concluded that pyrolysis at higher temperature can lead to pyrolytic carbon production and diminished their mechanical properties [12]. The ultimate tensile strength of the rCF can be affected, hence dependent on the final pyrolysis temperature.

3.4 Surface morphology analysis

The surface morphology analysis of rCF as compared to CFRP as control were shown in Figure 4. It clearly showed that the polymer was attached with the surface of carbon fibre before the pyrolysis process [13]. The polymer acted as the protective cover to reduce the damage to carbon fibres. The polymer sizing was also observed on the surface of carbon fibre of CFRP. The surface of pure CFRP was clean and smooth without any crack or fissures. The diameter of carbon fibre for CFRP was in he surface morphology of rCF after pyrolysis with final heating temperature of 550°C were analyzed (Figure 4). The rCF were seen free of contaminant residues on their surfaces. The resin on the carbon fibres has also been removed with the sizing and shape of rCF were maintain. Means, at the final temperature 550°C, able to reclaim the carbon fibre from CFRP at good condition. Meanwhile, at both final pyrolysis temperature of 600°C and 650°C, the fracture initiates and propagates along the interface between adjacent internal layers near the specimen midplane [14]. Fracture surface of the fibre were coated with resin, more cracks in the resin with fragments scattered around it can be noticed. The diameter of carbon fibres was decreasing with irregular shapes, revealed that the carbon fibres had been damaged. The surface analysis of both rCF at 600°C and 650°C also showed many groove marks.

4.0 CONCLUSION

Reclaiming carbon fibres by pyrolysis was performed best at final temperature 550℃. The rCF were seen free of contaminant residues and resin on their surfaces with the sizing and shape of rCF were maintain at this temperature. Strength of rCF showed that pyrolysis was greatly proposed to reclaim carbon fibres from CFRP. Pyrolysis at higher temperatures can lead to more pyrolytic carbon production and diminished mechanical properties and affect the ultimate tensile strength of the rCF. Further analysis on the effect of a combination of this rCF with another natural fiber is suggested for future secondary structural application of the rCF.

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