THERMAL DECOMPOSITION ANALYSIS OF HIGH END APPLICATION WASTE CURED CARBON FIBRE REINFORCED POLYMER FOR SECONDARY INDUSTRIAL APPLICATION

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Abstract

This paper examines the recovery of carbon fibers (CF) from a polymeric composite waste of high end application industry. Thermolysis technique and gasification in nitrogen coupled with oxygen atmosphere is applied by particularly studied the influence of different process parameters (final heating temperature, atmosphere and heating rate). Thermal decomposition analysis of the high end application CFRP waste cured carbon fibre was studied by thermogravimetric analysis (TGA). The samples were heated in dual environment of nitrogen (420⁰C) and oxygen (540⁰C) at different heating rate (5 and 10⁰C/min). Visual inspection was performed with SEM and FT-IR, respectively to assess the morphological properties and chemical composition of the recovered CF. Molecules of epoxy resin components were found to decompose in nitrogen atmosphere followed by complete matrix decomposition in oxygen atmosphere. Lower heating rate at 5⁰C/min efficiently separate the left reclaimed carbon fibre from their matrix. The different system of CFRP from industrial waste required different recovering methods of CF.

Keywords: CFRP, Epoxy resin, Thermolysis, Recycling, TGA
I. Introduction

CF have been used increasingly as valuable reinforced material in the composite especially in the high-end application industry, targeting lightweight but strong materials such as aero composite. Their widespread use, meanwhile, generates a large amount of waste of such CF-reinforced polymer (CFRP) which end-up at the landfills. By 2030, more than 6000 commercial planes will reach their expiration date and will contribute to high end application CFRP waste at the landfills. Thus, recycling the high end CFRP waste become necessary and highlighted among researchers to decrease environmental problem due to increasing waste at the landfills and high possibility for secondary structural application in the automotive and medical area.

CFRP complex formulation generally includes a resin matrix, strengthen in gmaterials and complex composite. This composition make the CFRP waste is difficult to decompose in bulk and need for thermal decomposition analysis since every CFRP waste has unique chemical properties and thermal decomposition system. Recycling offers the possibility to produce recovered CFRP (rCFRP). This recovered CF have been applied in numerous parts of automotive, due to their unique behavior which can be recycled without drastically loosen its excellent properties. Due to environmental regulations, the above demand of recovered CF has become a boost for recycling manufacturing waste from carbon-base industry. Waste from carbon-base recycled via thermolysis has been attracted due to promising method and cost reduction process incurred for the recycling of composites, especially when recovering high valuable products of CF. Pickering has reported earlier that thermal decomposition technique is promising to eliminate the complex composite of CFRP waste and produce reclaimed-CF. However, through this technique, the CF produced was reported to show almost 20% strength reduction compared to virgin CF. Fabrication and manufacturing optimization of recovered CF has been studied.

Heating rate is one of the important heating profile to be examined in thermolysis technique to assess the degree of variation associated with kinetics. The thermal decomposition profile will shift the mass loss peaks to higher temperature significantly with the increment in heating rate. Higher heating rate encourage the production of volatiles and favors competitive reactions. Therefore, this work aim to study on the thermal decomposition technique of high end application waste cured CF at different environment and different heating rate. Once suitable conditions were achieved, the recovered CF were analyzed via morphological and chemical approach to further ensure the recovering of 60% CF in CFRP by eliminating completely the complex epoxy resin.

II. Materials and Methods

Materials

High end application waste cured carbon fibre reinforced polymer provided by Composites Technology Research Malaysia was used as raw material. The prepreg waste reinforced with 60% CF.
Thermo Gravimetric Analysis (TGA)

TGA were conducted on Mettler Toledo brand of TGA with nitrogen and oxygen purge gaseous at 50mL/min. Samples were heated from 250 to 420°C in nitrogen, holding at 420°C in nitrogen for 30 mins and continue heating to 800°C at different heating rate (5 and 10°C/min).

Surface and Chemical Analysis

Scanning electron microscopy (SEM) was conducted to study the mechanism of action of thermal decomposition process and morphological properties of CFRP (control) and reclaimed-CF. FT-IR spectroscopy (JASCO FT-IR, 6100), in a range of 400 to 4000 cm\(^{-1}\) via ATR method was used to observed any chemical reaction occurred.

III. Results and Discussion

Thermal Decomposition Atmosphere

Fig. 1 shows TGA analysis of CFRP thermal decomposition at different environment of nitrogen and oxygen. In this study, inert pure gases like nitrogen and oxygen were used to analyzed the thermal decomposition process. Both nitrogen and oxygen environment were found to show significant weight loss when the samples were heat-up until 1000°C. But, the pattern of the decomposition reaction is slightly altered for both atmospheres. The first highlighted area (Fig. 1A) reveal a single main decomposition step in nitrogen atmosphere, which occurred at ~240 to 500°C, and continue become flat for heating >500°C . The final residual weight at 1000°C is high at 72.7%. Oxygen environment shows two main decomposition steps observed as highlighted in Fig. 1(A and B). The first decomposition step occurred at ~236°C and second decomposition step occurred at ~at 716°C. As compared to nitrogen atmosphere, the final residual weight for oxygen atmosphere is lower at 68.5%.

![Fig. 1: TGA analysis of CFRP at different environment reveals (A) 1\(^{st}\) decomposition step and (B) 2\(^{nd}\) decomposition step for oxygen environment.](image-url)
As highlighted in Fig. 1 (A), the decomposition step occurred for both environment was accredited to the breakdown of complex resin matrix. In nitrogen environment, increasing of temperature cause carbonaceous residue covering the reclaimed-CF to form due to resin carbonization. High residue of CFRP at temperature ~506.65°C is allocated an organic-based sizing compound decomposition of CFRP only. Hence, nitrogen atmosphere only can significantly decomposesizing and part of complex resin and left the solid reclaimed-CF with many resin residue. Even at 1000°C still high residue (72.70%) were left shows ineffectiveness of elimination of complex CFRP resin matrix and incomplete separation of reclaimed-CF. While, in oxygen environment only, increasing of temperature decomposed complex resin matrix and start to burn everything except reclaimed-CF and produce carbonaceous residue at 236.94 to 506.65°C (Fig. 1A). Hence, higher weight loss is revealed for oxygen environment at ~400°C is attributed to the macromolecules decomposition due to covalent bonds breaking. However, it is suggested that reclaimed-CF is start to decompose at the second decomposition step around ~716°C for oxygen environment. As compared to nitrogen, oxygen environment is observed to give more effect in the CFRP thermal decomposition.

Thus, it can be concluded that single environment in thermal decomposition process is not efficient. Decomposition process should completely eliminate complex resin matrix and produced separated individual reclaimed-CF at a quality near the virgin CF. Oxygen environment is not significant at the early stage of decomposition, since it burns out all to carbon residue as described by Tranchard et al. Oxygen is needed to completely burn resin matrix residues at higher temperature only, while nitrogen is needed to breakdown complex resin matrix at the early temperature. In agreement, Meyer et al. also claimed first step of decomposition occurred at ~250 °C in nitrogen followed by a second step at ~500 °C in oxygen environment. The reclaimed-CF maintained more than 95% of tensile strength with completely elimination of complex resin matrix. Combination of environment is essential to produce reclaimed-CF via thermal decomposition technique.

Analysis of Heating Rate Influence

The thermogravimetric (TG) curve of the CFRP for 5 and 10°C/min of heating rate were compared in Fig. 2. In this study, the dual environment of nitrogen followed by oxygen was applied. Both samples reveal slow decomposition until ~245°C. Here, first decomposition step occurred (Fig. 2A) until 420°C. Then, second decomposition step occurred until ~550°C for heating rate of 10°C/min and ~538°C for heating rate of 5°C/min. Increasing in temperature revealed another significance difference between 5 and 10°C/min heating rate. The TG trend for 10°C/min However, at higher temperature (>500°C), different trend reveals when the TG curve for CFRP of 10°C/min shifted to 50°C higher temperatures as compared to 5°C/min heating rate. Heating rate of 5°C/min completed it process with almost ~0 wt% residues at 620.58°C, while heating rate of 10°C/min completed it process at 671.62°C with the same amount of residues.
Fig. 2: TGA analysis of CFRP at different heating rate shows 3 main decomposition step of A, B and C.

Fig. 2 (A-C) shows the DTG curve of CFRP at different heating rate (5 and 10°C/min) that reveals 3 main decomposition phases: i) at ~245-250°C, ii) at ~420°C and iii) at ~540-550°C. The highest decomposition rate of ~1.25 wt.%°C⁻¹ at temperature of ~600°C was observed for 5°C/min heating rate and 1.0 wt.%°C⁻¹ at temperature of ~650°C for 10°C/min. Efficient removal of 40% complex resin matrix and left 60% of reclaimed-CF was experienced for 5°C/min heating rate. While, higher weight residues was observed for 10°C/min (62.39%). So, lower heating rate significantly influence thermal decomposition process of CFRP.

Autocatalytic reaction can be one of the possible reason for the 10°C/min higher temperature of thermal decomposition completing process as compared to 5°C/min. The gases evaporated during thermal decomposition process can trigger the reaction to be occurred. For example, NH₃ emission is suggested to promote decomposition of CFRP and acidic gaseous promote the breakup of covalent bond. Higher heating rate that tends to produce gases and volatiles will moves the whole thermal heat flow to more endothermic, which can be seen clearly happened at process temperature >540°C. Thus, it indicates that these gases emitted from the resin decomposition act like a catalyst and stimulate again the decomposition process. Here, low heating rate is suggested in thermal decomposition process of CFRP as the autocatalytic reaction is low and the burning process can be controlled to avoid recovered-CF damage.

Hence, referring to TGA of 5°C/min, it can be suggested that, ~540°C is the best final heating temperature for thermal decomposition of CFRP before the recovered-CF start to decompose. The final weight residues at ~540°C for 5°C/min heating rate was 60%, which is similar to the weight% of CF by volume for the raw material. Means, by using this heating profile; 5°C/min, dual environment nitrogen and oxygen and final heating temperature of 540°C, the complex resin matrix of CFRP can be eliminate efficiently to produce recovered-CF.
Morphology Properties of Reclaimed-CF

Fig. 3 shows the morphological properties of the recovered-CF as compared to CFRP after TGA at different heating rate. For this morphological study, final heating temperature of 540°C was applied. From the surface analysis, CFRP (control) shows a compact and almost flat surface (Fig. 3A (i-ii)). Generally, both heating rate result in separated and individual recovered-CF free from their complex resin matrix (Fig. 3bi and 3ci). However, at higher magnification, the surface analysis of recovered-CF were significantly shows different result. 10°C/min heating rate left many fractured residues on the recovered-CF surfaces while maintained their size around ~8μm in diameter (Fig. 3bii). 5°C/min heating rate produced much clean and smooth recovered-CF surfaces with the similar diameter in size (Fig. 3cii).

Many fractured residues surrounded the recovered-CF from the 10°C/min heating rate might be due to complex resin matrix that do not decomposed completely during thermal decomposition of CFRP. Supported by TGA earlier, 10°C/min heating rate gave slightly higher final residues (~62%) at ~540°C as compared to 5°C/min (60%). The weight% by volume around ~2% might be the fractured residues scattered along the recovered-CF surfaces. This infers slower heating rate is more efficient in eliminating the complex resin matrix of CFRP.

Referring to the cross sectional analysis of in Fig. 4, different heating rate also gives significant effect in terms of their structure. Virgin CF diameter are mostly in range of 6 to 10μm. Control (Fig.4a) contained CF with diameter in the range of 6.5 to 7.7 um, embedded in complex resin matrix (Fig.4b). The recovered-CF for both 5 and 10°C/min shown similar in size with control. However, 10°C/min (Fig.4c) was found to have groovy end-surfaces and shrank spherical shape of recovered-CF. While 5°C/min (Fig.4d) produced nice spherical shape with compact end-surface.
Even the size is smaller compared to control due to removal of complex resin matrix.

**Fig. 4:** Cross-sectional analysis of (a) CFRP (control) and recovered CF after thermal decomposition at heating rate of (b) 10°C/min and (c) 5°C/min

**Mechanism of Thermal Decomposition**

Fig. 5 shows thermal decomposition mechanism of CFRP represents morphological analysis of CFRP decomposition stages (Fig. 5A) coupled with TGA of CFRP decomposition (Fig. 5B). The samples were heat up in nitrogen atmosphere from 250 to 420°C followed by oxygen atmosphere from 420 to 540°C.

**Fig. 5:** Thermal decomposition mechanism of CFRP: A) step by step SEM micrograph of CFRP thermal decomposition, B) TGA of CFRP thermal decomposition and C) schematic diagram of control cross-sectional

During first decomposition step in nitrogen environment at ~250°C, the structure of CFRP was found still compact and strong. CF is still tightly bonded to each other embedded in complex resin matrix. Next, second decomposition step produced looser complex resin matrix but with still tightly bonded bundle of CF with. Finally, after 540°C, clear recovered-CF that separated from each other is observed.
Temperature 540°C in oxygen environment is recognized as the final heating temperature to produce recovered-CF and removed efficiently the complex resin matrix.

Apparently, there are three significance decomposition phases. Elimination of complex resin matrix is a slow and long process in nitrogen environment. As illustrated in Fig. 5, nitrogen environment is essential part that contribute to the breakup of large molecules matrix into smaller molecules without degraded the CF. Still, some pyrolytic carbon (residue) are still remained scattered on the CF surfaces. Further heated in the nitrogen environment aimed to remove the complex resin matrix totally. Oxygen purged with very slow heating rate at 2nd decomposition stage (~420°C), the complete burning of pyrolytic carbon occurred until final heating temperature of 540°C. Fig.5 reveal a separated recovered-CF at final heating temperature. Meyer et al. reported that in the air environment, the entire complex resin matrix can be removed within the temperature range from 580 to 600°C. Based on the results presented, this study suggests that 540°C enable to do so and further heating will cause degradation of recovered-CF.

**FT-IR Analysis of CFRP Decomposition Phase**

FT-IR analysis aim to study chemical reaction through thermal decomposition process. Fig. 6 shows the essential functional groups that decomposed throughout the thermal decomposition process. 3 main decomposition step figured out from TGA were nominated. The main FT-IR features for control including O-H and CH₂ functional group of epoxy at ~3400 cm⁻¹ and ~2900 cm⁻¹ respectively. While C=O (~1600 cm⁻¹), C=C (~1550 cm⁻¹) and C-H (~850 cm⁻¹) corresponding to epoxy resin were also observed. Directly after 1st and 2nd decomposition phase, of all those epoxy important peaks were disappeared without any substitution. Finally, recovered-CF after 3rd decomposition phase shows complete absence of all important functional groups and left only C FT-IR pattern recognized as recovered-CF.

**Fig. 6:** Chemical analysis of CFRP thermal decomposition

Complex resin matrix from high end application industry possess strong bonding and high mechanical and thermal properties. This strong bonding can be breakup in
nitrogen atmosphere. Changing environment to the oxygen while continue heating complete the burning process of complex resin matrix gently and efficiently. A final heating temperature in the range of 500–550 °C appears then to be the high limit of the thermal decomposition process in order to maintain acceptable strength for CF and this type of technique appears therefore to be improved to recover CF as revealed and supported by FT-IR analysis in this study.

IV. Conclusion

Thermal decomposition method with specific heating profile consist of environment, heating rate and final heating temperature is suggested to be efficient technique to recover CF from CFRP waste. Oxygen does not influence the decomposition of the resin at the early temperature. Combination of nitrogen atmosphere at the early temperature with oxygen atmosphere at higher temperature is needed to achieve a complete separation of CF from their matrix and maintaining their reinforcement capability. Lower heating rate of thermal decomposition efficiently burn out the complex resin matrix to produce clean recovered-CF. Further morphological and chemical analysis done by SEM and FT-IR supported the mechanism of CFRP decomposition process.

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