博士論文

Research on carbon fiber mat reinforced thermoplastics for advanced use of recycled carbon fibers

(リサイクル炭素繊維の高度利用のための炭素繊維マット強化熱可塑性樹脂に関する研究)

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論文の内容の要旨

Thesis Summary

論文提目　Research on carbon fiber mat reinforced thermoplastics for advanced use of recycled carbon fibers
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Carbon fibers reinforced composites have been applied in aerospace, wind power generation, automotive and sport facilities industries. There is a large amount of products made of carbon fiber reinforced composites have met the end of their lives. Even though landfilling is a strategy to deal with these wastes, there are more and more law regulations requiring companies to recycle the CF from them. Therefore, researches of recycling CF from correlative wastes has been a hot topic recent years. Several studies have confirmed that current available recycling technologies are able to maintain the rCF (recycled carbon fiber) with promising mechanical properties. And even some recycling technologies are practically commercial now.

The undamaged rCF compared with fresh CF has the characteristics in morphology: shortened fiber length distribution (FLD) and misaligned fiber orientation distribution (FOD). The aim of this research, using papermaking technology is to fabricate rCF with matrix resin fibers and to discuss solutions to the problems of reusing rCF: mixed different types of rCF and addition of a secondary reinforcement fibers.

Before discussing the effect of mixing different fiber types, the proper compression molding pressures and the basic material properties of CPT materials were discussed. After comparing the flexural properties under 5 levels of compression molding pressure, 1 MPa, 3 MPa, 5 MPa, 8 MPa and 10 MPa, were investigated.　The flexural properties of CPT reinforced by R-T300 (recycled T300 fibers) and CPT reinforced by R-T800 (recycled T800 fibers) are good during 3 MPa and 8 MPa. After further discussion of the results of Izod tests, the impact energy absorption is highest under 5 MPa and 8 MPa. Therefore, it is recommended that the molding pressure should be set from 5 MPa to 8 MPa.

In order to increase the cost-benefit efficiency of reusing rCF, alignment process is necessary

to be introduced into re-manufacturing process. Even though there are a few studies proposing alignment concepts, they cannot be used into mass-production due to the lack of proper assessments of reinforcement efficiency and alignment degree of misaligned discontinuous CFRTP. In this thesis, two indexes were introduced.

The first one is the reinforcement efficiency factors, Factor Cs, which is derived from the modified rule of mixtures (MRoM). Based on the experiment results of three point bending tests and component material properties, the Factor C_1 of flexural modulus and C_2 of flexural strength were also calculated. In order to discuss the value of Factor Cs, carbon fiber card web reinforced thermoplastics (CWT) made by a carding process were used to investigate the flexural properties. Based on the continuous movement of carding process, the molded CWT plates were different in mechanical properties along the L-direction (moving direction) and along T-direction. Based on the calculations, Factor Cs are suitable to illustrate the internal fiber architectures due to different manufacturing process by removing the interference of component material properties and that of volume fraction (V_f) of the components. In order to further extend the value of Factor Cs, a development map was built based on Factor Cs of different materials by considering the isotropic and anisotropic properties. The map is able to help the manufacturers to understand where their products locate among the similar materials in market. Additionally, this map can help to adjust the alignment process, which is a critical process in manufacturing rCF, in a direct way.

The second index is the alignment degree. Even though the Factor Cs can contribute to developing the manufacturing process and the relative rCFRTP materials, they are negatively affected by the internal defects, such as void content. Therefore, a new index is needed to identify the quality of alignment process in re-manufacturing rCF. In thesis, a simple quantitative value was introduced based a two-parameter exponential equation. Different from conventional qualitative approach, the alignment degree can be used to connect the FOD of rCFRTP materials with the alignment quality, mechanical properties and V_f in an analytical way. A brief discussion was conducted to compare the Factor Cs and the alignment degree. Factor Cs are more practical to guide the development of rCFRTP materials and help to describe the possible mechanical properties based on relative manufacturing process. Alignment degree is more practical to determine the quality of alignment process. One single value made it possible and analytical to compare the FOD of different materials by different alignment processes.

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Abbreviation list

CF	Carbon Fibers
GF	Glass Fibers
rCF	Recycled Carbon Fibers
CFRP	Carbon Fiber Reinforced Plastics
CFRTS	Carbon Fiber Reinforced Thermosets
CFRTP	Carbon Fiber Reinforced Thermoplastics
CPT	Carbon fiber Paper reinforced Thermoplastics
Mix-CPT	CPT including various volume fraction ratios of different rCF types
CPT(rCF/GF)	CPT including rCF and glass fibers (GF)
CWT	Carbon fiber Card Web reinforced Thermoplastics
S-CWT	Stretched CWT materials
FLD	Fiber Length Distribution
FOD	Fiber Orientation Distribution

Chapter 1. Introduction

1.1 Research background

The global demand for carbon fibers (CF) is increasing annually, as shown in Figure 1-1 [1]. CF are promising materials of high elastic modulus, high tensile strength, low density, high chemical resistance and high thermal resistance [2]. CF are almost 5 times lighter but 4 times stronger compared with steel, the conventional structural material. Therefore, CF are increasingly applied to make the structural parts for airplanes, wind power generators and automotive vehicles [1] [3] .

In order to increase the fuel efficiency and to improve the aerodynamic performance, airplane companies put more and more attention on advanced light materials, such as aluminum, titanium and CF [4]. Even though the cost of CF is still higher than steel, it has been decreasing in the last decade. Decreasing price of CF will extend the corresponding applications in automotive. BMW group launched BMW i3 – electrical city car and BMW i8 – hybrid sports car in late 2013. Especially, BMW i3 applies a large amount of CF and are sold at a price point reachable by general consumers [5]. Stimulated by the BMW i-series launch, the demand of CF for vehicles will be increased.

In order to meet the possible upsurge of CF demand, a joint venture was founded between the BMW Group and SGL Group, in 2009, for the supply of carbon fiber materials to the BMW Group. In 2013, Toray Industries, Inc. acquired Zoltek in order to supply CF to automotive market. Toray industries has since entered an extension contract with Boeing to extend the supply duration of CF for the next generation of airplanes, demonstrating the increased demand for CF. The production of CF is predicted to reach 140,000 Mgt by 2020 [6].

Generally, CF have to be used with impregnation of matrix resin, which is termed as carbon fiber reinforced plastics (CFRP). Conventionally, thermosets are used as matrix resin because of low viscosity, high mechanical properties and high temperature tolerance. Carbon fiber reinforced thermosets (CFRTS) were originally used in aerospace and airplanes. However, the disadvantages of CFRTS include long molding cycle and difficulty in recycling development. After the retirement of first generation of airplanes partly applying CF, investigations of recycling CF have been in the center of attention from both research and industry fields. At almost the same time, thermoplastic resin has been considered to be promising as matrix resin in CFRP materials because of promising recyclability, resistance to chemicals, ability to be repair, re-melt and re-processed [7] [8] [9] [10] [11]. Additionally, carbon fiber reinforced thermoplastics (CFRTP) are considered practical because of the advantage of fast molding cycle. Combined the situations of researches of recycling CF from CFRP wastes and of CFRTP materials, recycled carbon fiber reinforced thermoplastics (rCFRTP) are considered to be secondary supply for CF demand and they will contribute to decrease the price of CF.

However, there are problems of re-manufacturing recycled carbon fibers (rCF) including: randomly orientated fiber arrangement, shortened fiber length and contamination problems (e.g. mixed different rCF types and mixed with other reinforcement fibers) [12].

1.2. Introduction of carbon fibers and the applications

1.2.1. Introduction of carbon fibers (CF)

CF are made from precursors by pyrolysis process and of diameter of 5-10 μm. Donnet and Bansal reviewed several researches about various precursors including polyacrylonitrile (PAN), pitch, phenol, imides, rayon, and etc. [13]. Originally, the demand of CF has increased from 1980s due to the improved aerospace and sporting goods industries. In the 1990s, Zoltek and Frtaril companies increased the cost-efficiency of manufacturing PAN-based CF and then the application of CF has been extended in markets [14]. Various manufacturers are currently supplying CF for material markets. The capacity to produce the small-tow CF for aerospace applications is dominated by the fiber companies, as shown in Table 1-1. The CF capacities by manufacturers in 2013 as shown in Figure 1-2.

PAN-based CF are manufactured by production processes composed by polymerization, spinning, oxidation, carbonization, graphitization, surface treatment and sizing. The oxidation process is critical in CF manufacturing because it determines whether high-quality CF would be obtained [15] [16] [17]. During the spinning process, the internal structures of CF will be more aligned and increasing the anisotropic properties of CF. CF are generally supplied in the form of continuous tow as shown in Figure 1-3.

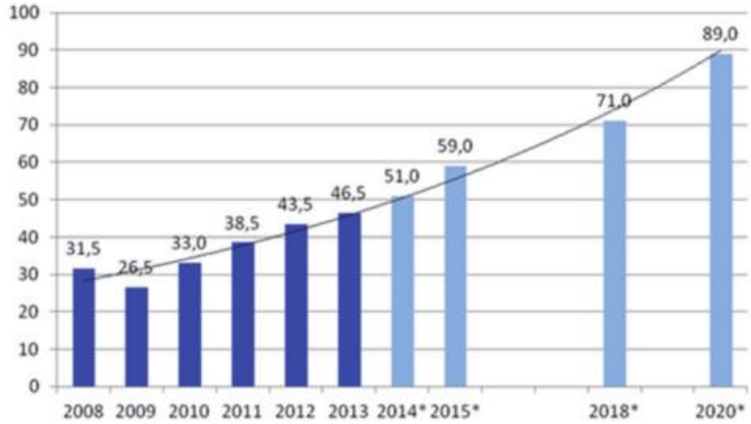


Figure 1-1 Global demand for carbon fiber in thousand tonnes 2008-2020 (*estimated) [1]

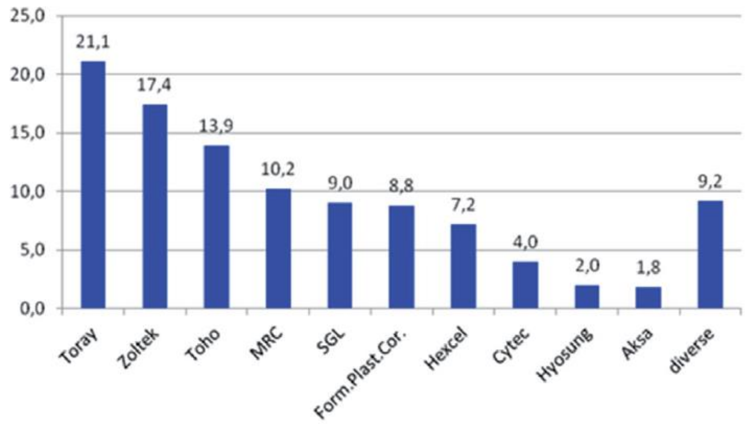


Figure 1-2 CF capacities by manufacturer in thousand tonnes (2013) [1]

Figure 1-3 A photo of carbon fibers (CF)

Table 1-1. Summary of capacity and locations of the top five small-tow carbon fiber producers [5]

CF supplier	Capacity 2012 vs 2020 (tonnes/yr)	Precursor	Fiber	Prepreg	Aerospace Customers/Programs*	Comments
Toray	18,900 vs. 50,000	Ehime, Japan; Decatur, AL, United States; Abidos, France	Decatur, AL, United States; Abidos, France; Ehime, Japan; Gumi, South Korea	Tacoma, WA, United States Japan	Boeing 787 Airbus	60% aviation market share
Toho Tenax	15,100 vs. 18,900	Shizuoka, Japan	Shizuoka, Japan; Oberbruch, Germany	Shizuoka, Japan	Bombardier CSeries, A380	Thermoplastic focus Airbus contract
Mitsubishi Rayon	10,600 vs. 14,300	Okake, Japan	Otake, Japan; Toyohashi, Japan; Sacramento, CA, United States	Irvine, CA, United States	A380	Largest acrylic fiber producer in Japan
Hexcel	7,250 vs. 10,000	Decautur, AL, United States	Salt Lake City, UT, United States; Illescas, Spain	United States; Europe: Tianjin, China	Airbus A350 A380	47% of 2007 sales driven by Boeing and Airbus
Cytec	2,400 vs. 6,000	Piedmont, SC, United States	Piedmont, SC; Rock Hill, SC	Tempe, AZ, United States; Greenville, TX, United States	Bombardier F-35 COMAC C919	Boeing 787 uses infusion resins and surface treatments including prepregs by Cytec

1.2.2. Carbon fiber reinforced plastics (CFRP)

CF cannot be directly used as fibrous status, because they are weak in resistance against compression although they have promising tensile properties along fiber axis. Generally, plastic resins are introduced as matrix for CF composites in order to hold the CF against compression and additionally to transfer the stress of neighboring fibers between each other. Carbon fibers reinforced plastics (CFRP) are commonly manufactured for product parts in aerospace, blades of wind power generators, automotive vehicles and sporting goods [5] [1].

After the commercialization development of CF, epoxy or polyester resin of thermoset plastics are commonly used as matrix resin. Carbon fiber reinforced thermosets (CFRTS) are, until now, generally used in aerospace and wind power generation industries. However, during the development and applications of CFRTS products, thermoplastic plastics are also applied as matrix resin for CFRP materials [18] [19] [20], which is called as carbon fiber reinforced thermoplastics (CFRTP). Therefore, there are two main categories of CFRP materials depending on the matrix resin types: CFRTS and CFRTP.

The differences between thermoset and thermoplastic resins are listed in Table 1.1. Different from the irreversibly curable thermosets, thermoplastic polymers are capable of being re-melted, repaired and re-processed after heating. Despite the advantage of thermally reversibility, high durability, elastic modulus, electrical conductivity and fast molding cycle. Among them, fast molding cycle is critical to drive the development and commercialization of CFRTP products [18].

Table 1-2 The difference between thermoset composites and thermoplastic composites

	Thermoset composites	Thermoplastic composites
Molding cycle (Cost)	Long (Expensive)	Short (Cheap)
Formability of complex parts	Difficult	Easy
Compatibility with discontinuous fiber	Bad (Brittle)	Good (Ductile)
Compatibility with CFRP recycling	Bad	Good

1.2.3. Manufacturing methods for CFRP materials

For composites manufacturing processes, there are three main categories: open molding, closed molding and cast polymer molding [21]. Included in the three categories, closed molding is generally applied. There are various sub-categories in closed molding: vacuum bag molding, vacuum infusion processing, resin transfer molding, compression molding, pultrusion, reinforced reaction injection molding, centrifugal casting and continuous lamination. Broadly speaking, there are three approaches for CFRTS and two for CFRTP [22], as shown in Figure 1-4.

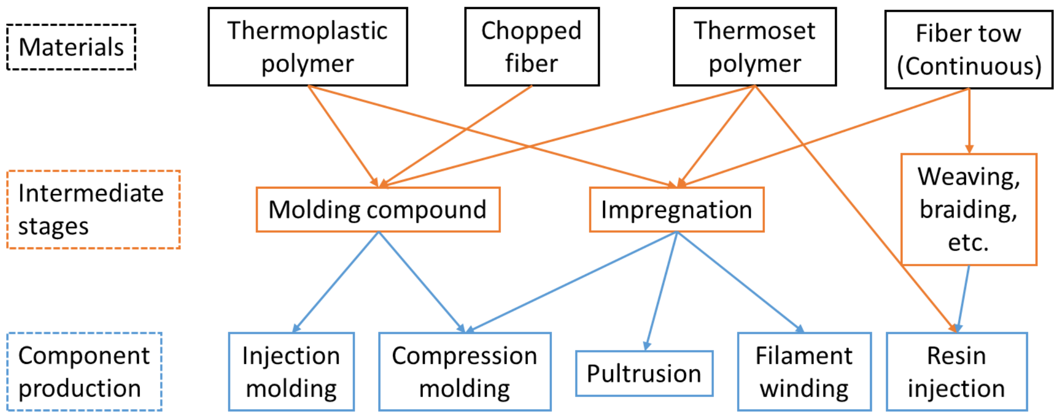


Figure 1-4 Schematic overview of the approaches employed in fabrication of polymer matrix composites [22].

1.3. Recycling of CFRP materials

1.3.1. Current status of CFRP wastes

After decades of development and applications, a lot of products including those in aerospace, wind power generation and automotive industries made by CFRP have met their ends of lives. Landfilling is a common way to solve the problem of retired CFRP products. However, the disposal regulations for these kinds of wastes are becoming much stricter in some European countries [23]. Therefore, it is urgent to solve the problem that more and more CFRP wastes from four main sources as shown in Figure 1-5. The four sources of CFRP wastes include out-of-date pre-preg rolls, manufacturing cut-offs, yatch mold and end-of-live aircraft wings. Several researches of recycling technologies have realized the potential value of the CF in CFRP wastes. Therefore, recycling technologies have been developing for several years. Not only the feasibility but also the cost-benefit are considered during the researches of recycling technologies both in scientific and market areas [24] [25].

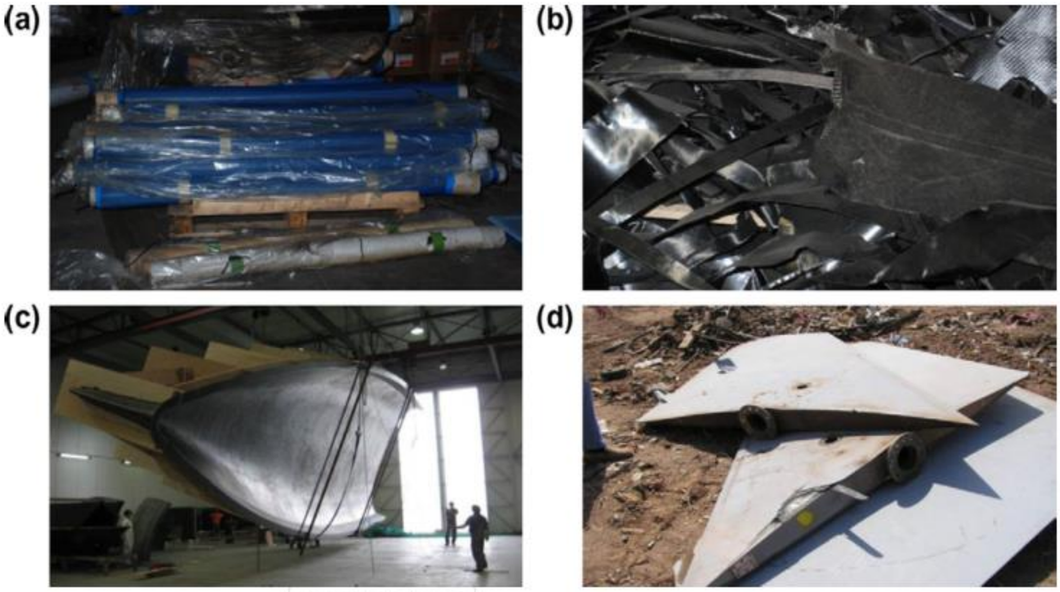


Figure 1-5 CFRP waste. (a) Out-of-date pre-preg rolls. (b) Manufacturing cut-offs. (c) Yatch mould. (d) End-of-live aircraft wings [24] [26]

1.3.2. Current recycling technologies

Based on current characteristics of recycling technologies, the CFRP wastes must be decreased in size during pre-processing and recycling steps. The recycled carbon fibers (rCF) will be discontinuous in length and misaligned, as shown in Figure 1-6. Some studies have demonstrated that recycled carbon fibers (rCF) maintain high elastic modulus and strength, comparable to those of fresh CF [23][27].

However, there several problems of recycling composites caused by (i) complex composition (different reinforcement fibers, matrix and fillers), (ii) difficulty of removing thermoset plastics, (iii) hybridized with other structures or materials (metal fixings, honeycombs, hybrid composites, etc.), (iv) difficulty of sorting and separating the wastes, (v) damages due to furious recycling processes, and (vi) deterioration of mechanical properties of filaments after recycling [25].

There are two main categories of recycling processes: mechanical recycling and thermal processes, as shown in Figure 1-7. Thermal processes are more favorable due to irreversibility of thermoset plastics, which are generally applied in CFRP products. As illustrated by Pimenta et al. [24], it will decrease the cost-benefit efficiency to scale up the recycling process into commercial scale. Therefore, the investigations of recycling CFRP materials have to focus on the cost efficiency. Table 1-3 simply summarized the chemical recycling technologies in Japan. In this thesis depolymerization under ordinary pressure was conducted because ordinary atmosphere pressure and lower temperature can ensure promising manufacturing costs.

Figure 1-6 A photo of recycled carbon fibers (rCF)

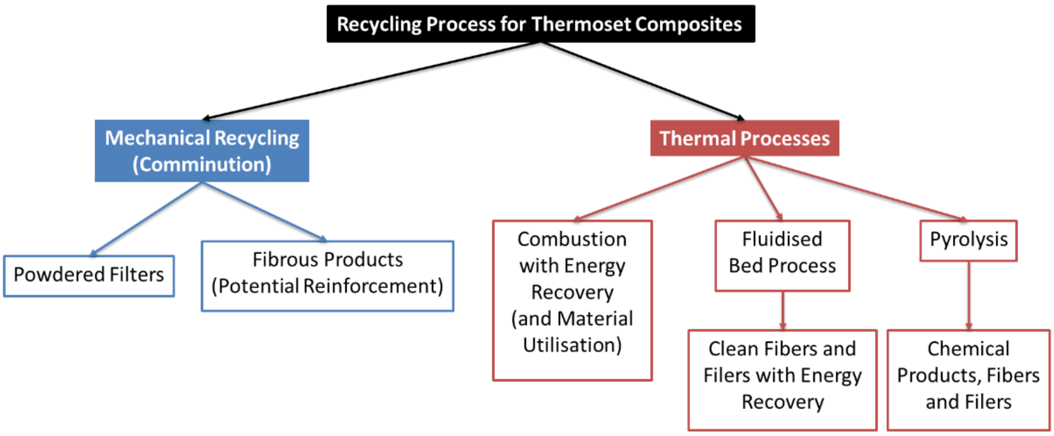


Figure 1-7 Recycling processes for thermoset composite materials [25]

Table 1-3 CFRP chemical recycling in Japan [40]

Item	Thermal decomposition		Supercritical fluid technique	Subcritical fluid technique	Depolymerization under ordinary pressure
Organization	Toray Industries Teijin Mitsubishi Rayon	Takayasu	Shizuoka University	Kumamoto University	Hitachi Chemical
Temperature	500-700 ℃	Not known	250-350 ℃	300-400 ℃	200 ℃
Pressure	Ordinary pressure	Ordinary pressure	5-10 MPa	1-4 MPa	Ordinary pressure
Solvent	-	-	Methanol	Benzyl alcohol	Benzyl alcohol
Catalyst	-	-	None	Alkali metal salt	Alkali metal salt
Preprocessing	Pulverization	-	Pulverization	-	-
Processing capacity	1,000 tons/year	60 tons/year	(5 L)	(0.5 L0	12 tons/year (200 L x 2 baths)

1.3.3. Problems of re-manufacturing recycled carbon fibers (rCF)

After recycling the CF from CFRP wastes, there are several problems hindering the development of re-manufacturing rCF roughly shown in Figure 1-8.

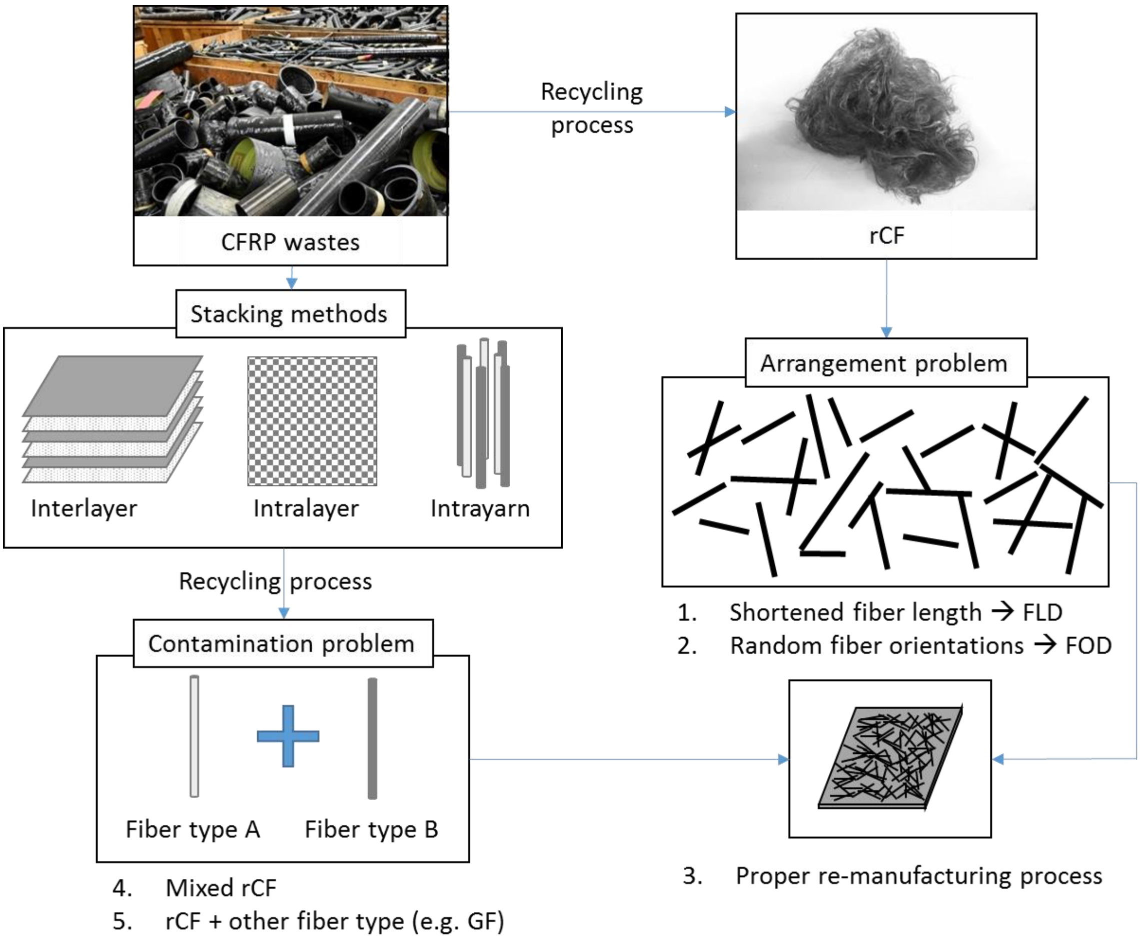


Figure 1-8 Schematic problems in reusing rCF

1.3.3.1. General problems of rCF

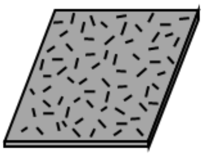
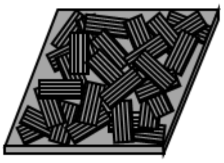
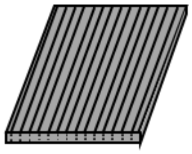
Conventionally, unidirectional CFRTP are the most applied material form for structural materials. The volume fraction (V_f) of CF can be over than 50%. Due to the anisotropic properties of CF, the mechanical properties of continuous laminates of CFRP are very promising along the fiber direction. Different from unidirectional continuous laminates, there is another type of CFRTP material composed by unidirectional CF reinforced tapes, the name is chopped carbon fiber tape reinforced thermoplastics.

There have been several studies to investigate different recycling processes. Current recycling technologies can ensure that Young's modulus of fibers will not be damaged and the tensile strength can be maintained of 80% compared with fresh CF. However, the differences between fresh CF and rCF are about the fiber length distribution (FLD) and the fiber orientation distribution (FOD). The FLD and FOD of fresh CF are continuous and unidirectional but those of rCF are discontinuous and random.

However, based on the characteristics of rCF, the FLD is not long enough for continuous laminate but is longer than the FLD of injection molding. Based on the fiber length distribution of CF, the CFRTP materials can be classified into four categories: injection molded materials, mat structure thermoplastics, chopped carbon fiber reinforced thermoplastics and continuous laminates, as shown in Table 1.4. Due to the characteristics of injection molding, the fiber length distribution (FLD) of injection molded CFRTP materials is lowest. Additionally, the V_f of CFRTP is lowest. Therefore, injection molding cannot be used as manufacturing process for structural materials.

Furthermore, fiber orientation distribution (FOD) of rCF is randomly orientated, which makes the mat structure thermoplastic suitable to be the media to reapply rCF. The volume fraction range is from 20% to 30%.

Table 1-4 CFRTP composite forms based on fiber length distribution (FLD)

FLD	Low	Middle	High	Highest
Type of composite system	Injection molded 	Mat structure thermoplastics 	Chopped carbon fiber tape reinforced thermoplastics 	Continuous laminates 
Volume fraction (V_f)	Relatively low	Middle (20-30%)	High (>50%)	High (>50%)
Formability	Superior	General	Superior	Directional dependent
FOD	Process dependent	Process dependent	Designable	Designable

1.3.3.2. Contamination concerns

The varied kinds of rCF are recycled from a variety of commercial CF products made by many companies, including Toray Industries, Toho Tenax, Zoltek, Mitsubishi Rayon Co., Ltd., and Hexcel. Specific market requests require the production of different fresh CFs with higher modulus or higher strengths. It is a problem to use these rCF in a balanced way.

As shown in Figure 1-9, the contamination problem is due to the stacking methods when industries designed the products in a complex way. In current aerospace, wind power generation and automotive industries, the CFRP materials are composed or laminated by several types of CF. Current sorting technologies and processes cannot separate them. Additionally, the characteristics of recycling technologies and processes cannot help to sort different reinforcement fibers.

There are two types of contamination problem. The first one is that different CF types have been mixed before recycling and the second one is that mixture of CF and another kind of reinforcement fibers, such as glass fibers (GF).

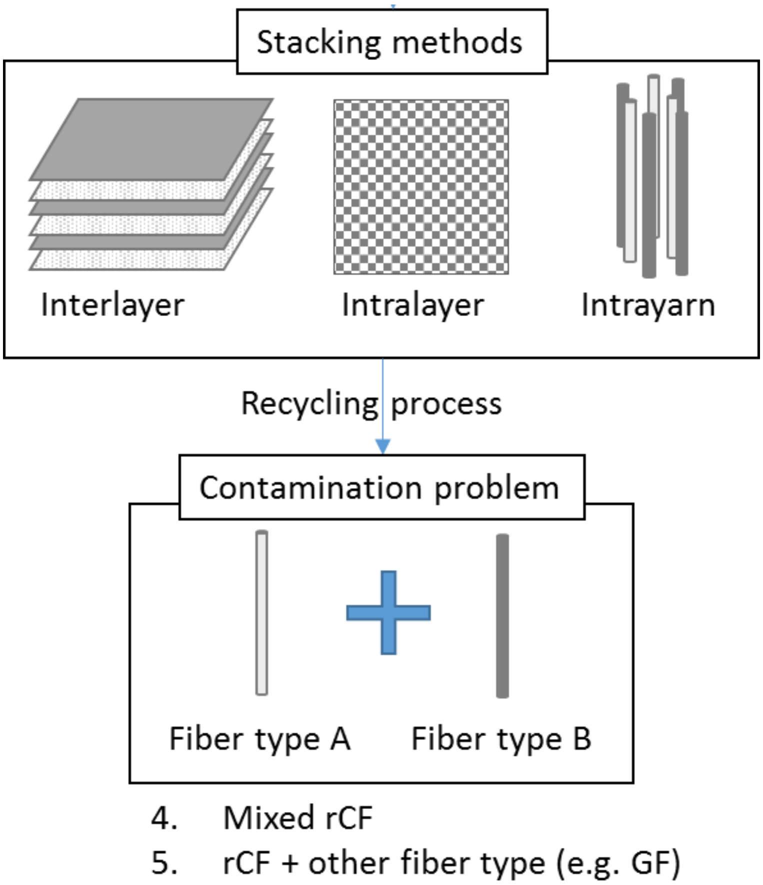


Figure 1-9 Schematic contamination problem

1.3.4. Further steps of re-manufacturing rCF

1.3.4.1. Prediction of reinforcement efficiency

Currently, manufacturing processes of mat structured composites are more proper to re-fabricate rCF. Figure 1-10 shows the internal fiber architecture of mat structured composite. Different from CFRP materials including fresh CF, which is unidirectional and continuous fibers, rCF in mat structured materials randomly oriented and discontinuous status. FOD and FLD discussed in Section 1.3.3.1 are critical factors affecting the mechanical properties of rCFRTP materials. Due to the anisotropic properties of CF, the reinforcement efficiency will be damaged if the FOD of fibers is randomly distributed. Therefore, determination of reinforcement efficiency is a critical problem need to be discussed.

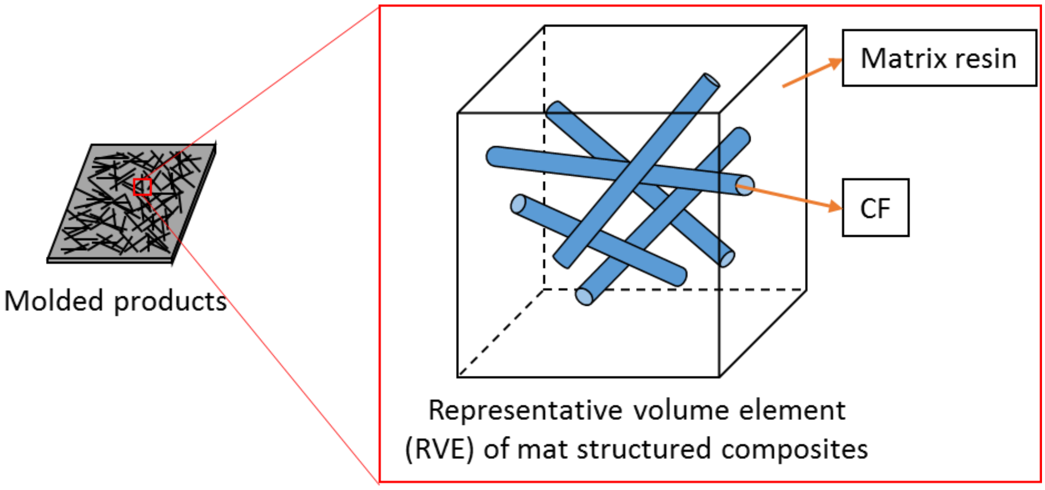


Figure 1-10 Schematic of internal fiber architecture of mat structured composites

1.3.4.2. Alignment process and alignment degree

Described in Section 1.3.3.1, current re-manufacturing processes can use rCF to make mat structured composites. However, the V_f of final products is no more than 40% because of the discontinuous FLD and misaligned FOD. If the rCF can be aligned along with the same direction, not only the V_f can therefore be increased but also the mechanical properties of products can be enhanced along the fiber alignment direction. The aligned rCF can be used for extended applications, such as chopped carbon fiber tape reinforced thermoplastics (CTT), as shown in Table 1.2, the V_f of which can be over than 50%. CTT materials have been confirmed to be promising both in higher mechanical properties and more flexible product designs. Therefore, alignment process will be a critical step for further development of rCFRTP materials.

In order to determine the alignment quality of alignment process, a determination index is necessary to guide the development of alignment process. The common approach is based on statistical analysis, which qualitatively determines the shape of FOD. However, it is problem if we want to connect specific processing parameter with FOD because the connection can only be explained by description in language. A quantitative index, alignment degree in this thesis, is necessary to solve the barriers, as shown in Figure 1-11.

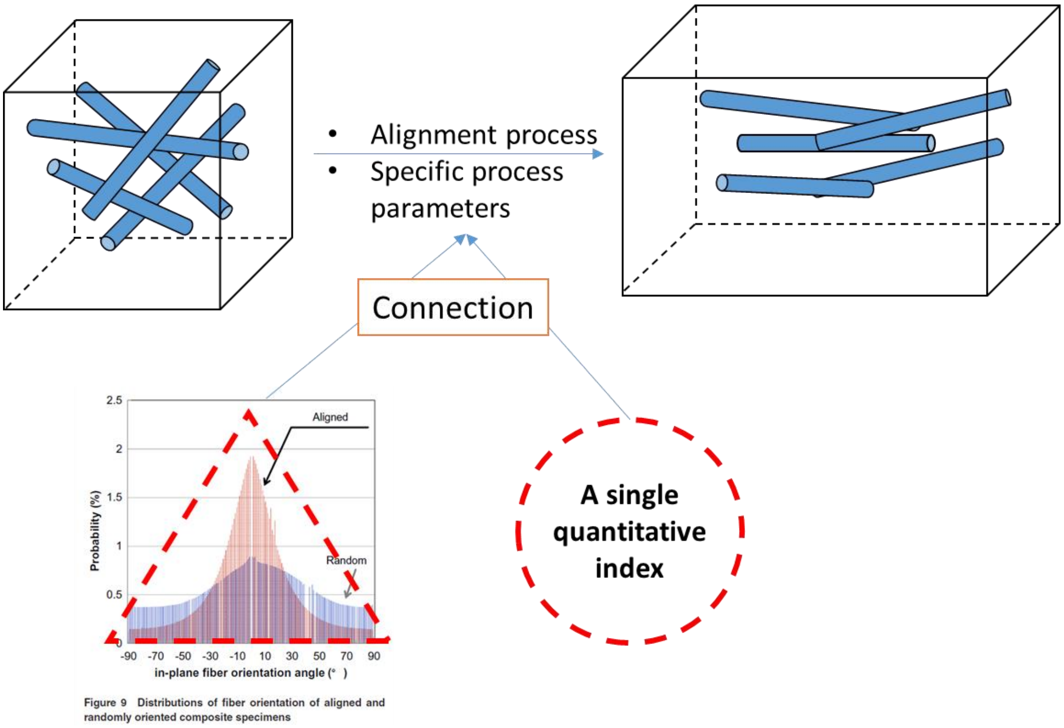


Figure 1-11 Quantitative determination of FOD for alignment process

1.4. Research goals and outline of thesis

The structure of this thesis is shown in Figure 1-12.

i. In this study, we introduced a papermaking process to produce carbon fiber paper reinforced thermoplastics (CPT). rCF through depolymerization under ordinary pressure were used.

ii. In order to extend the applications of rCF in a more balanced way, two types of CPT materials were introduced. One is made by mixing two types of rCF and the other is by mixing rCF with GF.

iii. A modified rule of mixture was introduced to obtain reinforcement efficiency factors, Factor Cs.

iv. A new definition of alignment degree based on a two-parameter exponential equation is proposed.

Chapter 1: Introduction

- Current application of CFRP
- Introduction of re-manufacturing rCF
- The problems of reusing rCFRTP
- The purpose of this thesis

Chapter 2: A papermaking process to investigate re-manufacturing problems

- Introduction of papermaking process
- Determination of compression molding pressure
- The problems of reusing rCFRTP

Chapter 3: Reinforcement efficiency index – Factor Cs

- A modified rule of mixture
- A continuous carding process
- Factor Cs of different materials
- Development map built on Factor Cs

Chapter 4: A quantitative definition of alignment degree

- A two-parameter exponential equation
- A definition of alignment degree
- Alignment degree and material properties

Chapter 5: Summary

Figure 1-12 The main content of each chapter in this thesis

Chapter 2. A papermaking process to investigate re-manufacturing problems

2.1. Papermaking process

rCF are randomly oriented and discontinuous status due to current barriers of sorting procedures and recycling technologies. Thus, how the re-manufacturing rCF is the first problem needs to be solved.

In conventional manufacturing process, the first step is to fabricate the reinforcement fibers and then the fabricated fiber web will be impregnated by resin films. In this study, the resin fibers will be fabricated with reinforcement fibers at the same step, as shown in Figure 2-1. The second step in this study is to mold the fabricated preforms. Therefore, the manufacturing steps in this study can be reduced by one step and then the manufacturing cost will be decreased.

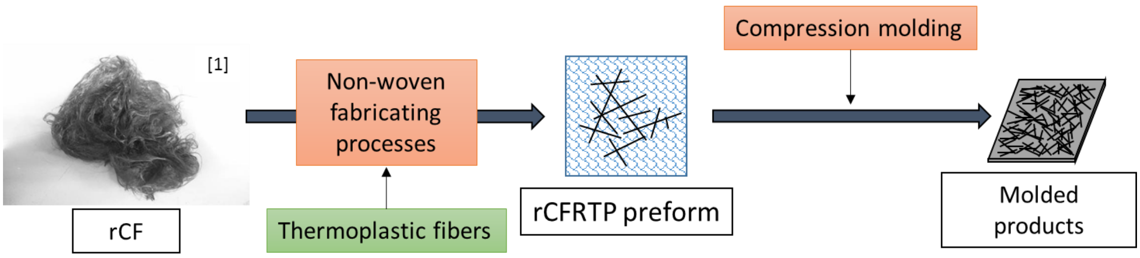


Figure 2-1 Schematic flowchart of re-manufacturing concept for rCF

2.1.1. Introduction of papermaking technologies

The following description is from Wikipedia.org about basic concept of papermaking process:

"In papermaking, a dilute suspension consisting mostly of separate cellulose fibers in water is drained through a sieve-like screen, so that a mat of randomly interwoven fibers is laid down. Water is further removed from this sheet by pressing, sometimes aided by suction or vacuum, or heating. Once dry, a generally flat, uniform and strong sheet of paper is achieved [27]*."*

2.1.2. Why papermaking process is suitable for rCF

During the process of waste disposal, separations and recycling processes, CF in CFRP wastes will be decreased in length and redistributed in orientations. Originally, CF will be manufactured continuously. Because CF is much more promising along fiber direction and weaker in transverse direction, CF can realize their full mechanical potential by arranging the fibers unidirectional. However, unidirectional CFRP sheets are generally applied by crossed stacking due to the request of load transfer. Cross plied CFRP sheets induce the difficulties for recycling. There is no practical method to reclaim the reinforcement fibers with keeping their original morphologies, FOD and FLD. Randomly oriented and shortened rCF hinder the current possible manufacturing methods to re-fabricating them in promising way, such as fabricating rCF into aligned fiber arrangement. Therefore, it is critical to reuse the mechanically available rCF of random FOD and FLD.

Papermaking process introduces water as dispersion agent to distribute cellulose fibers in order the make papers of uniform areal densities. Water dispersion can increase the momentum to actuate fiber movement and orientation change. After careful stirring, the fibers will be uniformly located. The mechanism of papermaking process is therefore to be applied to fabricate rCF. As mentioned above, rCF are shortened and misoriented, therefore it is important to disperse rCF uniformly. The consideration of uniformly dispersing rCF is not only to improve the areal densities of resultant sheets but also to ensure the impregnating quality.

Impregnation is a critical step during manufacturing CFRTP materials. Different from thermoset resin, thermoplastic resins is more viscous, which will hinder the thermoplastic resin wetting the network of rCF. Additionally, network of randomly oriented rCF will increase the barrier positions that will negatively affect the movement of resins. Therefore, uniform dispersion of rCF is critical during material development.

Above all, papermaking process is a promising way to uniformly disperse fibers, which is necessary to develop the applications of rCF.

2.1.3. The papermaking process introduced in this thesis

Compared with the traditional carbon fiber mat-reinforced plastics, the matrix is fiber-shaped in order to shorten the impregnating distance, which solves the reinforcing problems caused by the high viscosity of thermoplastics. By careful stirring during the papermaking process, rCF can be uniformly oriented and the fiber length can therefore be protected from molding.

The characteristics of rCF is the discontinuous FLD and misaligned FOD. The both characteristics request the re-manufacturing process to be modified. In this research, a papermaking process was used to re-manufacture rCF.

The papermaking process used in this research, the thermoplastics resin fibers and the rCF will be directed poured into a container of water, as shown in Figure 2-2. After careful stirring, the mixture of thermoplastic rein fibers and rCF will be uniformly dispersed. The water will be drained and the mixture sheet will be let on mesh. The carbon fiber paper reinforced thermoplastics (CPT) sheets are like in Figure 2-2.

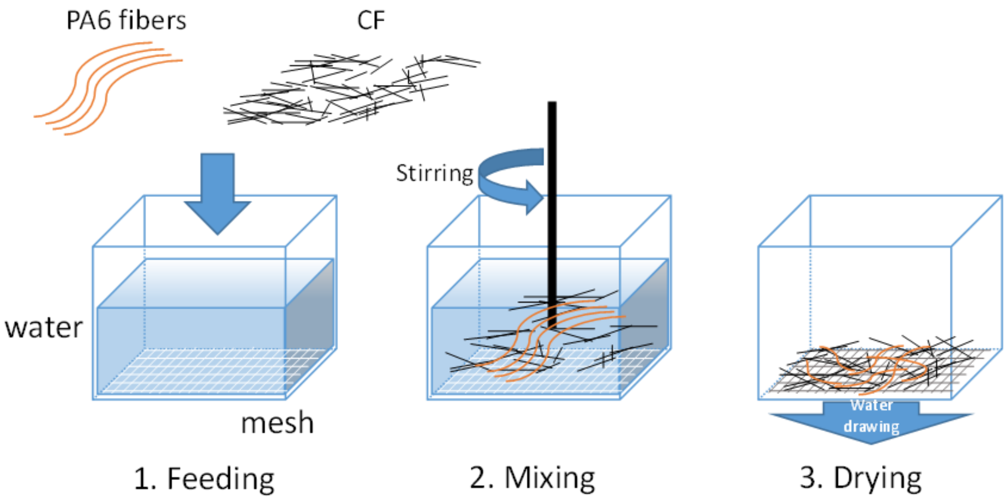


Figure 2-2 A schematic image of papermaking process

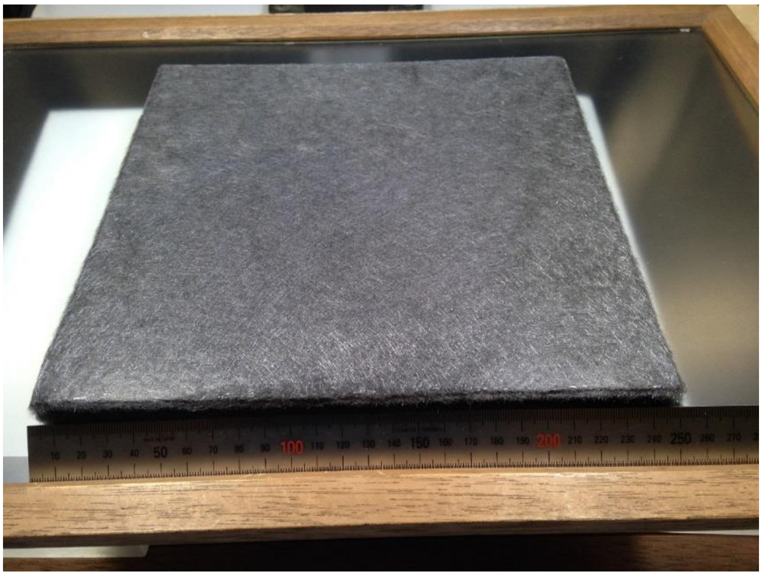


Figure 2-3 A photo of carbon fiber paper reinforced thermoplastics (CPT)

2.2. Research outline of this Chapter

2.2.1. Investigation flowchart

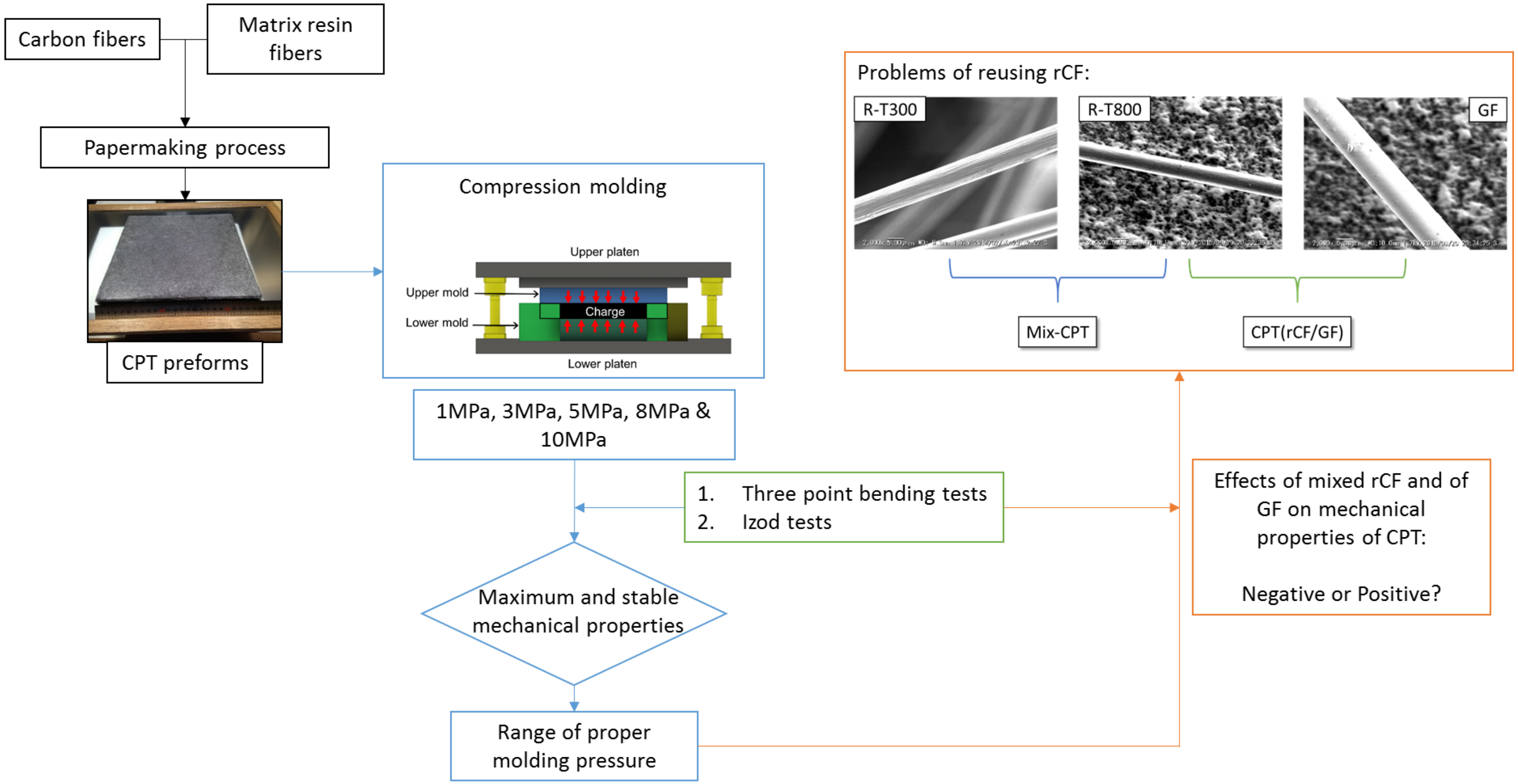


Figure 2-4 Investigation flowchart of this chapter

2.2.2. Observations and mechanical experiments approaches

2.2.2.1. Ash tests

The specimens were cut by the length 15 mm and the width of 10 mm. An MDS-300 electronic densimeter (Alfa Mirage Co., Ltd., Osaka, Japan) was used to measure the density of the specimens and an AUX320 electronic balance (Shimadzu Corp., Kyoto, Japan) was used to measure the weight of specimens before and after the ash tests. An oven shown in Figure 2-5 was used for the ash tests, for which the temperature was set to 550 ℃ and the heating time was 1-1.5 h. The real volume fraction (V_f) ofrCF was calculated by Eqn. (2.1)

$$V_f = \frac{m_1 \rho_c}{m_0 \rho_f} \tag{2.1}$$

Where m_0 and m_1 are the weights of the specimen before and after the ash test respectively, which are measured by an electronic balance of AUX320 from Shimadzu Co., Ltd. ρ_f is the density of the fiber, and ρ_c is the density of the specimen, which are measured by an electronic densimeter of MDS-300 from Alfa Mirage Co., Ltd.

Figure 2-5 An oven for ash tests

2.2.2.2. Microscope observation

A digital microscope of VHX-1000 from Keyence Cooperation, as shown in Figure 2-6, is used to check the surface of specimens.

Figure 2-6 A digital microscope of VHX-1000 from Keyence Cooperation

2.2.2.2. Scanning electron microscope

We use scanning electron microscope (SEM) to observe the fracture surface of specimens after Izod tests. The machine of VE-8800 is provided by Keyence Cooperation, as shown in Figure 2-7.

Figure 2-7 A scanning electron microscope of VE-8800 from Keyence Cooperation

2.2.2.3. Three point bending tests

Three point bending tests following the JIS K7017 standard with a span of 32 mm were conducted to investigate the flexural modulus, strength, and failure strain of the CPT. The specimens were investigated for each test. The testing machine, as shown in Figure 2-8, was an AUTOGRAPH AG-X tabletop universal testing machine (Shimadzu Corp., Kyoto, Japan). The crosshead speed is 1 mm/min.

The flexural stress is calculated by Eqn. 2.2.

$$\sigma = \frac{3PL}{2bh^2} \tag{2.2}$$

Where σ is the flexural stress, P is the load, L is the span between two supports, and h is the specimen thickness.

The strain during bending is calculated by Eqn. 2.3.

$$\varepsilon = \frac{6Dh}{L^2} \tag{2.3}$$

Where ε is the failure strain, D is the maximum deflection of the center of the specimen, h is the thickness of specimens, and L is the span between two supports.

Figure 2-8 A table-top type of universal testing machine of AUTOGRAPHAG-X from Shimadzu Cooperation. Maximum load capacity: 5 kN; crosshead speed range: 0.0001-1000 mm/min

2.2.2.4. Izod impact tests

Izod tests following the JIS K7062 standard were conducted to investigate the impact energy absorption of CPT. The specimens were un-notched with widths of 10 mm and lengths of 50 mm, with thickness around 2 mm. Five specimens were investigated for each test using the Instron Dynatup POE2000e Impact Tester (Instron Corp., Norwood, MA, USA), as shown in Figure 2-9.

Figure 2-9 Instron Dynatup POE2000e Impact Tester. Maximum energy absorption capacity: 25.0 J.

2.3. Proper compression molding pressure range

2.3.1. Component materials

The CFRP wastes from aerospace are an important source of rCF. In original parts of airplanes, T300 and T800 fibers from Toray Industries are mainly used. Therefore, in this study, two types of CF were used, T300 and T800 fibers, which are from Toray Industries. Depolymerization under ordinary pressure conducted by Hitachi Chemical is introduced as recycling process. In order to clearly discuss the results, R-T300 and R-T800 are used to term the recycled T300 and T800 fibers. Polyamide 6 (PA6) fibers are used as matrix resin. The basic information of material properties are listed in Table 2-1. Figures 2−10 and 2-11 are the SEM pictures of R-T300 and R-T800 fibers. The averaged fiber length is around 6 mm due to the processing capacity of the papermaking process.

Table 2-1 Basic properties of the raw materials used in this study

	Density	Tensile modulus	Tensile strength	Failure strain
Materials	ρ (g/cm^3)	E (GPa)	σ_b (MPa)	ε_f (%)
T300	1.76	230	3530	1.5
T800S	1.80	294	5880	2.0
PA6 fibers	1.14	2	64	-

Note: T300: http://www.toraycfa.com/pdfs/T300DataSheet.pdf; T800: http://www.toraycfa.com/pdfs/T800SDataSheet.pdf

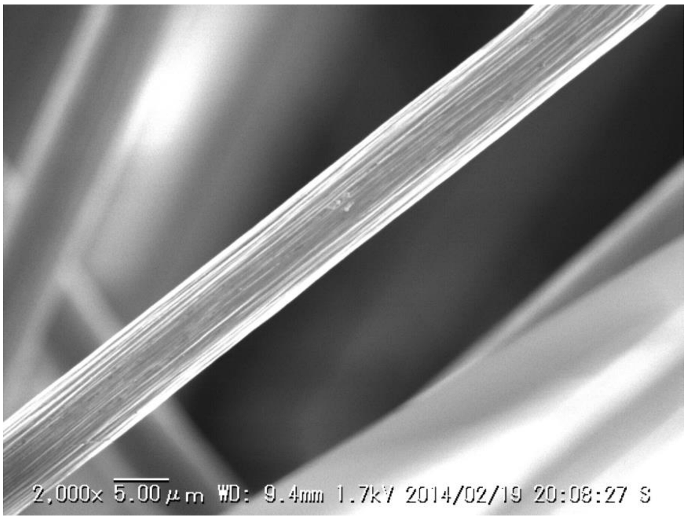


Figure 2-10 A SEM image of R-T300 fiber

Figure 2-11 A SEM image of R-T800 fiber

2.3.2. Compression molding procedures

The proper compression molding pressure for CPT is investigated. In the second part, an idea for mixing different kinds of rCF to reinforce thermoplastics is proposed.

In order to keep the molding conditions through this research, a research of proper molding conditions was conducted.

The molding temperature is 250 ℃. The melting temperature of PA6 is 230 ℃ plus 20 ℃ because there is temperature difference between compression molding machine.

The most concern in this research is molding pressure. In this research, we chose 5 levels of molding pressures, 1 MPa, 3 MPa, 5 MPa, 8 MPa and 10 MPa. The schematic image of compression molding process as shown in Figure 2-12

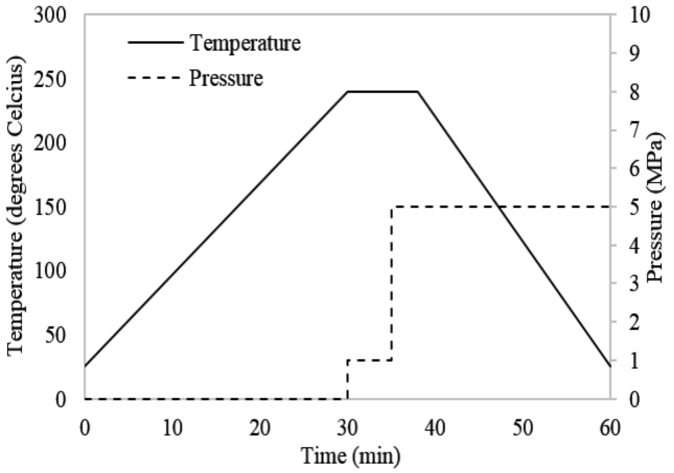


Figure 2-12 A schematic image of compression molding process

2.3.3. Observations

2.3.3.1. Ash tests

The real V_f of rCF under different compression molding pressures are listed in Table 2-2. As the molding pressure is increased, the V_f of CPT is also increased, reaching a maximum of 23%. While the expected V_f of CPT is 20%, PA6 wets the reinforcement fibers so easily that the fibers inevitably flow out of the mold at molding pressures exceeding 3 MPa. However, the maximum V_f occurs at lower molding pressures in this study. This is probably because of the amount of rCF lost with the resin flow. Therefore, the highest molding pressure (e.g. 10 MPa) is not necessary, while a very low molding pressure (e.g. 1 MPa) is not recommended.

Table 2-2 Real V_f and the specimen thickness for each molding pressure

	Specimen	1 MPa	3 MPa	5 MPa	8 MPa	10 MPa
V_f	R-T300/PA6	19%	21%	21%	23%	22%
	R-T800/PA6	19%	21%	21%	23%	22%
Thickness	R-T300/PA6	2.24	1.96	1.82	1.74	1.69
	R-T800/PA6	2.28	2.06	1.91	1.72	1.69

2.3.4.2. Observations through SEM

Figure 2-13 shows the SEM pictures of cross section of specimens for Izod tests. From Figures 2-13 (a) and (b), we can see that the interfacial adhesion between R-T300 fibers and PA6 is good enough. Different from CPT(R-T300), the interface between R-T800 and PA6 is less promising as shown in Figures 2-13 (c) and (d).

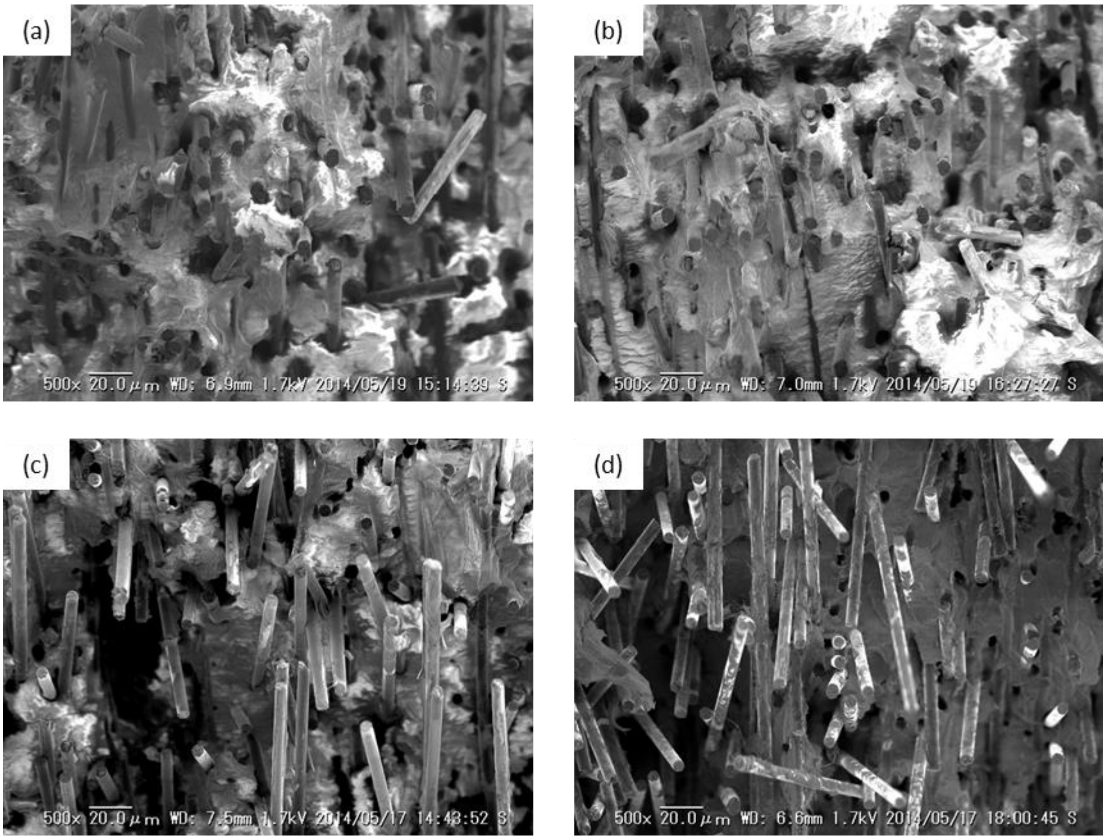


Figure 2-13 SEM images of surface of CPT: (a) CPT(R-T300) at 1 MPa; (b) CPT(R-T300) at 5 MPa; (c) CPT(R-T800) at 1 MPa; (d) CPT(R-T800) at 5 MPa

2.3.5. Results of mechanical properties

2.3.5.1. Three point bending tests

Figure 2-14 shows the flexural modulus of CPT calculated by the three-point bending tests. Regardless of the reinforcement composition, the flexural modulus is increased for increasing molding pressure up to 8 MPa. For pressures between 8 and 10 MPa, the modulus slightly decreases with increasing pressure. Additionally, for molding pressures of less than 8 MPa, the error bars of both R-T300/PA6 and R-T800/PA6 are smaller. This demonstrates that the papermaking process helps to disperse the fibers uniformly.

Figure 2-15 shows the flexural strength of CPT. For a molding pressure of 1 MPa, the flexural strength of R-T300/PA6 is 274 MPa and that of R-T800/PA6 is 358 MPa, showing a difference of 31%. With increasing the molding pressure to 3 MPa, the flexural strength reach 307 MPa and 461 MPa for R-T300/PA6 and R-T800/PA6, respectively, with the difference increasing to almost 50%. At molding pressures above 3 MPa, the flexural strengths vary only slightly for further increases in pressure. Furthermore, the error bars are similar for the same materials at molding pressures of 5 and 8 MPa.

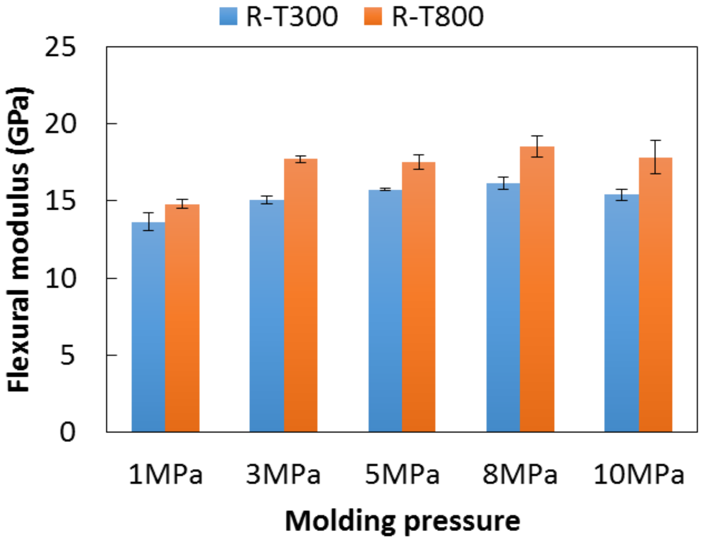


Figure 2-14 Results of flexural modulus of CPT materials under different molding pressures

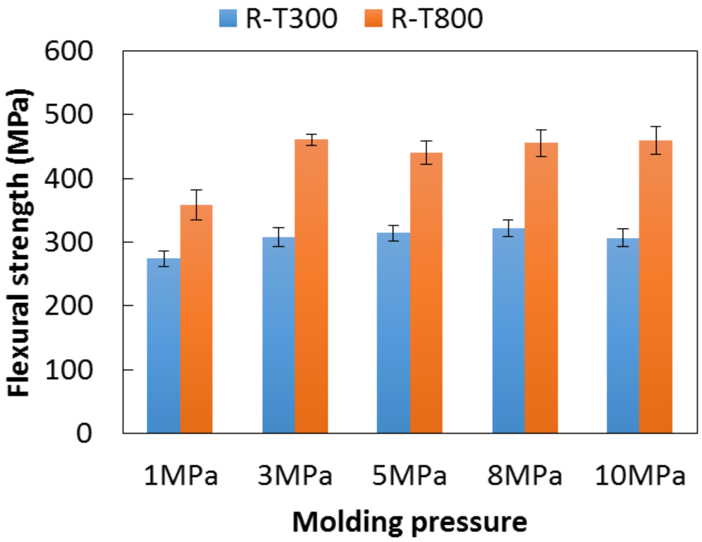


Figure 2-15 Results of flexural strength of CPT materials under different molding pressures

2.3.5.2. Izod tests

Although the increase in the failure strain indicates an increase in the potential energy absorption, the CPT fails via brittle fracture. As a result, the Izod impact energy absorption under different molding pressures shown in Figure 2-16 shows similar tendency of the flexural strength shown in Figure 2-15. For both R-T300/PA6 and R-T800/PA6, the highest absorptions occur at the molding pressure of 5 MPa, at 11.8 kJ/m^2 and 22.3 kJ/m^2, respectively. The second highest impact energy absorptions occur at the molding pressure of 10 MPa for R-T300/PA6 and R-T800/PA6. With higher V_f induced by the molding pressure of 10 MPa, more energy is absorbed. However, an overly high molding pressure also increases the damage to the rCF.

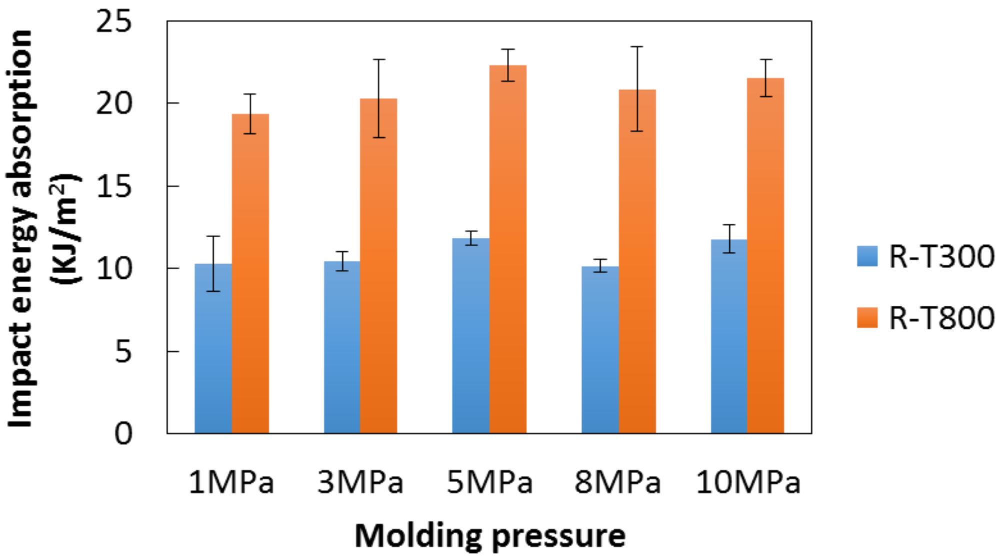


Figure 2-16 Results of impact energy absorption of CPT materials under different molding pressures

Table 2-3 Results of three point bending tests of CPT materials

Molding pressure	CPT (R-T300)						CPT (R-T800)					
	Flexural modulus (GPa)	CoV	Flexural strength (MPa)	CoV	Impact energy absorption (kJ/m^2)	CoV	Flexural modulus (GPa)	CoV	Flexural strength (MPa)	CoV	Impact energy absorption (kJ/m^2)	CoV
1MPa	13.6	4%	274	5%	10.3	16%	14.8	2%	358	7%	274	6%
3MPa	15.1	2%	307	5%	10.4	6%	17.7	1%	461	2%	307	12%
5MPa	15.7	1%	314	4%	11.8	4%	17.5	3%	440	4%	314	4%
8MPa	16.1	2%	322	4%	10.1	4%	18.5	4%	455	5%	322	12%
10MPa	15.4	2%	307	4%	11.8	7%	17.8	6%	460	5%	307	5%

2.3.5. Proper molding pressure range

When the molding pressure is between 5 and 8 MPa, CPT reinforced by either R-T300 or R-T800 fibers shows improvements in flexural modulus and strength relative to those at other pressures. Lower molding pressures induce impregnation defects, while higher pressures cause more fiber breakage and greater curvature of fibers. Among the specimens, CPT molded at 5 MPa showed the best Izod test results. Based on the discussion of this chapter, the proper molding pressure range is from 5 to 8 MPa.

2.3.6. Compare with published re-manufacturing processes

Table 2-4 shows several published re-manufacturing processes for rCF. Akonda et al. [28] modified a carding process and wrap spinning process to re-manufacturing process to align the rCF in order to extend the relative application capacity. Compared with the flexural properties of CPT materials at the molding pressure of 8 MPa, at which the flexural properties are highest as shown in Figures 2-14 and 2-15, the flexural modulus of composite C1 (V_f = 15%) and that of composite C2 (V_f = 27.7) are both higher than those of CPT(R-T300) and CPT(R-T800) materials. However, the flexural strength is much lower than CPT materials. Liu et al. [29] published a hydrodynamic alignment process, which is composed of rotating drum and vacuum pump. Even though the flexural properties and V_f of the specimens are very promising as shown in Table 2-4, the cost-benefit of scale-up process is not good. Because it needs high cost to enlarge the composition of rotating drum and vacuum pump for mass processi ng of rCF. The CPT materials are made by a papermaking process that is a mass production process. Therefore, it is not necessary to further enlarge the process level. There is a published re-manufacturing process for rCF based on existed industrial process proposed by Takushi et al. [30]. The mechanical properties are not promising enough to attract the attention from markets.

Therefore, the papermaking process introduced in this study is based on an existed mass paroduction process, which doesn’t need further enlargement.

Table 2-4 Compare with published re-manufacturing process of rCF

	Re-manufacturing method	Cost-benefit efficiency for scale-up	FOD	V_f (%)	Flexural modulus (GPa)	Flexural strength (MPa)
CPT(R-T300)	Paper making process	Good	Random	23	16.1	322
CPT(R-T800)				23	18.5	455
Akonda et al. C1 [28]	Modified carding and wrap spinning	Acceptable	Aligned	15	19	100
Akonda et al. C2 [28]				27.7	25	154
Liu et al. [29]	Hydrodynamic alignment process	Not good	Aligned	60	81.84 (L-direction) 7.23 (T-direction)	1247 (L-direction) 107.36 (T-direction)
Takushi et al. [30]	Modified yarn manufacturing process	Good	Random Aligned	13.3	3.6 (Tensile) 12.2 (Tensile)	38 (Tensile) 78 (Tensile)

2.4. Problems of re-manufacturing rCF

2.4.1. Current problems of re-manufacturing rCF

Recycled carbon fibers (rCF) will be increasingly used to fill the upsurge of the market requirement. However, rCF are usually contaminated by other kinds of fibers. Currently, the matrix materials for CFRP include thermoplastic and thermoset, both of which provide no change to recycle the CF from retired CFRP materials in much easier way. Additionally, rCF are usually contaminated by other kinds of materials, such as glass fibers (GF), which are usually used as hybridization fibers. But they are treated as contamination in rCF after recycling.

Over years of application, the toughness of CFRP has limited the extension in more structures. Therefore, hybrid composites have been investigated for years. In these researches, hybrid effect is defined as the increase of failure strain of hybrid composite compared with that of non-hybrid composite. In a recent review about hybrid composite materials, it is broadly accepted that the failure strain of the composite is increased by replacing some brittle CF with some ductile GF. Usually the brittle fibers are also referred as LE (Low elongation) fibers and the ductile fibers as HE (high elongation) fibers. Based on several simulations in some researches, the HE fiber adjacent to a broken LE fiber is able to bridge the matrix cracks caused by breakage of the LE fiber. Therefore, the failure of CFRP can be delayed by adding some ductile fibers, GF in this study.

Additionally considering the cost benefit, the strategies enhancing the low cost of application of rCF is helpful. Therefore, in this paper, the GF as contamination will not be primarily separated from the rCF.

In this study, three types of reinforcement fibers will be used to investigate the effect of mixed types of fibers on the mechanical properties of mat-structured CFRTP materials. As shown in Figure 2-17, two types of rCF were mixed to make mix-CPT and rCF mixed with GF were used to make CPT(rCF/GF) materials.

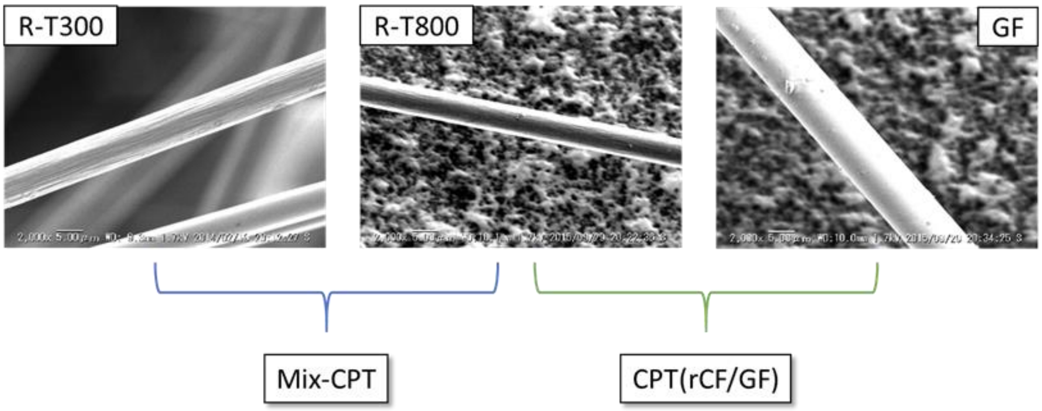


Figure 2-17 Combination of different fiber types

2.4.2. Mixed different types of rCF -- mix-CPT

2.4.2.1. Materials and compression molding conditions

Table 2-5 shows a series of volume fraction of R-T300 to R-T800. Here, the compression molding pressure has been determined at 5 MPa. The effects of the different V_f ratios of mix-CPT are presented by the results of mechanical properties investigations.

The basic information of material properties are shown in Table 2-6.

Table 2-5 The volume fraction ratio of R-T300 to R-T800

rCF/matrix	V_f of rCF	V_f ratio of R-T300 to R-T800
RCF(1.0/0.0)/PA6 (R-T300/PA6)	20%	1.0/0.0
RCF(0.8/0.2)/PA6		0.8/0.2
RCF(0.6/0.4)/PA6		0.6/0.4
RCF(0.4/0.6)/PA6		0.4/0.6
RCF(0.2/0.8)/PA6		0.2/0.8
RCF(0.0/1.0)/PA6 (R-T800/PA6)		0.0/1.0

Table 2-6 The basic mechanical properties of T300 and T800 fibers

Mechanical properties	T300	T800	Difference
Tensile modulus (GPa)	230	294	28%
Tensile strength (MPa)	3530	5880	67%
Failure strain (%)	1.5	1.9	27%

2.4.2.3. Mechanical properties of mix-CPT

In investigating mix-CPT to understand the influence of different mixture compositions and to propose a strategy for applying different kinds of rCF more efficiently, the compression molding pressure of 5 MPa was chosen.

From the results of testing different compression molding pressures, the flexural modulus of R-T300/PA6 formed at 5 MPa is 15.7 GPa; that of R-T800/PA6 is 17.5 GPa. The flexural strength of R-T300/PA6 fabricated at 5 MPa is 314 MPa; that of R-T800/PA6 is 441 MPa. Here, the investigation determines the variation in the mechanical properties of mix-CPT with different V_f ratios.

The results of the flexural modulus and flexural strengths of mix-CPT are shown in Figures 2-18 and 2-19, respectively. The modulus and strengths increase with increasing the volume of R-T800. According to the R-squared value, the flexural strength is much closer to a linear function of the amount of R-T800 than flexural modulus. T800STM fibers, used in critical structures, are produced to meet market requirements for high modulus and high strengths. Meanwhile, T300TM fibers are intended for relatively lower-performance products. The tensile modulus of T800STM is 28% higher than that of T300TM, but the tensile strength is 67% higher. Therefore, it is expected that the flexural strengths of the specimens will be improved more significantly by the addition of the stronger fibers.

Comparing the results of R-T300/PA6 and R-T800/PA6, the difference in flexural modulus using the results of R-T300/PA6 as reference data is just 11%, but that in flexural strength is 40%. Unlike tensile tests, both compressive and shear forces act on the specimens during three-point bending tests. CF is weak to compression and shear forces; both stresses can induce poor performance of CF with loading. Therefore, mixing R-T800 and R-T300 fibers is meaningful for market demands for higher-strength products. The range of flexural strengths provides many strategies for both high- and low-end products with greater flexibility. Accompanied with the low manufacturing cost of rCF, the mixture of different kinds of rCF, even without sorting, allows many application strategies during the product design stage.

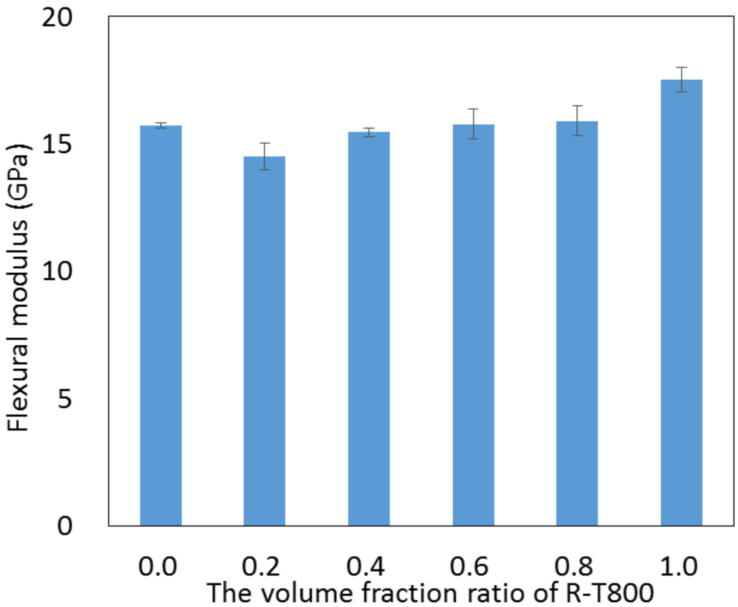


Figure 2-18 Results of flexural modulus of mix-CPT of different V_f ratio of R-T800 fibers

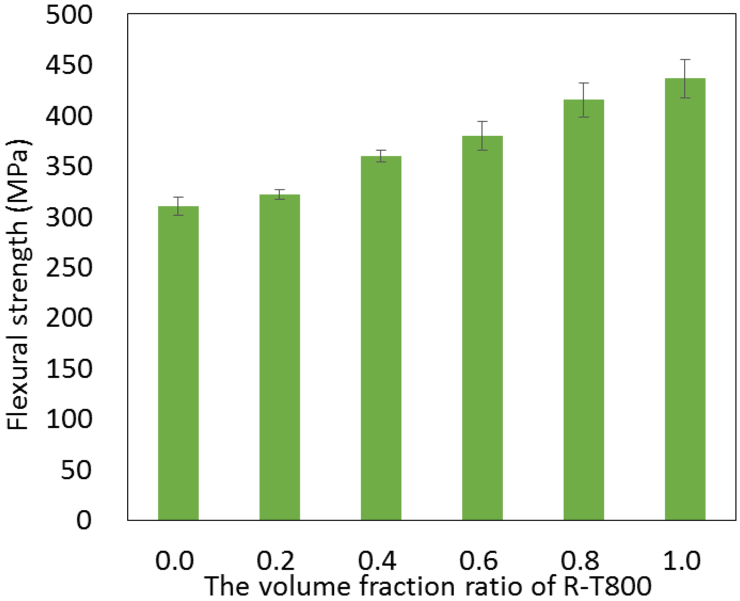


Figure 2-19 Results of flexural strength of mix-CPT of different V_f ratio of R-T800 fibers

Table 2-7 Results of three point bending tests of mix-CPT materials

V_f ratio of R-T800	Strength (MPa)			Failure strain (%)			Flexural modulus (GPa)			Impact energy (kJ/m^2)		
	Ave	Stdv.s	CoV	Ave	Stdv.s	CoV	Ave	Stdv.s	CoV	Ave	Stdv.s	CoV
0.0	314	11.927	4%	2.1	0.097	5%	15.7	0.106	1%	13.03	0.790	6%
0.2	322	4.960	2%	2.1	0.076	4%	14.5	0.513	4%	13.55	0.805	6%
0.4	360	5.857	2%	2.3	0.078	3%	15.5	0.152	1%	14.18	0.612	4%
0.6	380	14.293	4%	2.5	0.114	5%	15.8	0.582	4%	18.16	2.420	13%
0.8	415	20.152	5%	2.4	0.097	4%	15.9	0.582	4%	20.37	1.482	7%
1.0	441	18.115	4%	2.6	0.070	3%	17.5	0.484	3%	22.22	0.860	4%

2.4.3. Mixture of rCF and GF – CPT(rCF/GF)

2.4.3.1. Materials and compression molding conditions

Polyamide 6 (PA6) fibers are used as matrix, T800 fibers originally from Toray Industries Co. are recycled by means of depolymerisation technique of Hitachi Chemical Co., Ltd. Recycled T800 fibers are called as R-T800 in this study. The more details of the materials are in Table 1. Figure 2-20 shows the surface morphology of GF.

The papermaking technology was used to prepare the discontinuous recycled carbon fiber reinforced thermoplastics (rCFRTP). In this research, three levels of V_f of GF from 1, 2, and 5% were investigated and the related contaminated CPT will be called as CPT(rCF/GF1), CPT(rCF/GF2) and CPT(rCF/GF5), as shown in Table 2-8. The CPT(rCF/GF) preforms are shown in Figure 2-21.

Compression molding is chosen as the molding method. We chose the mold size as 110 mm in width and 110 mm in length. The molding pressure is 5 MPa and the molding temperature is 250 ℃.

Table 2-8 The volume fraction of the constituents of CPT (rCF/GF) materials

	Total V_f	V_f of GF	V_f of R-T800
CPT	20%	0%	20%
CPT-GF1		1%	19%
CPT-GF2		2%	18%
CPT-GF5		5%	15%

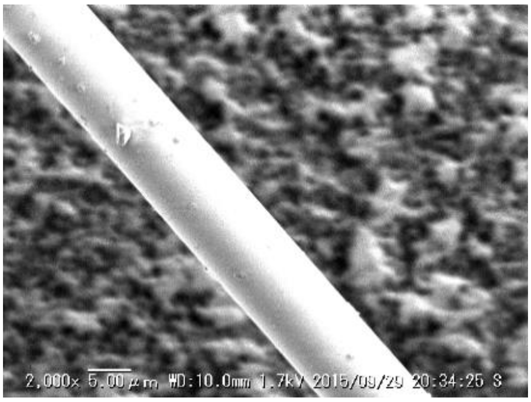


Figure 2-20 A SEM picture of glass fibers (GF)


Figure 2-21 A photo of CPT(rCF/GF)

2.4.3.2. Observations through microscope and SEM

A digital microscope of VHX-1000 from Keyence Cooperation will be used to observe the surface of the plates. Figure 2-22 shows the surface of the plates of CPT(rCF/GF1), CPT(rCF/GF2), and CPT(rCF/GF5). There are no significant voids observed from the surface. Therefore, 5 MPa is enough for CPT. The contamination of GF cannot be easy to be identified from the surface, so the appearance of CPT cannot be affected by the small amount of GF.

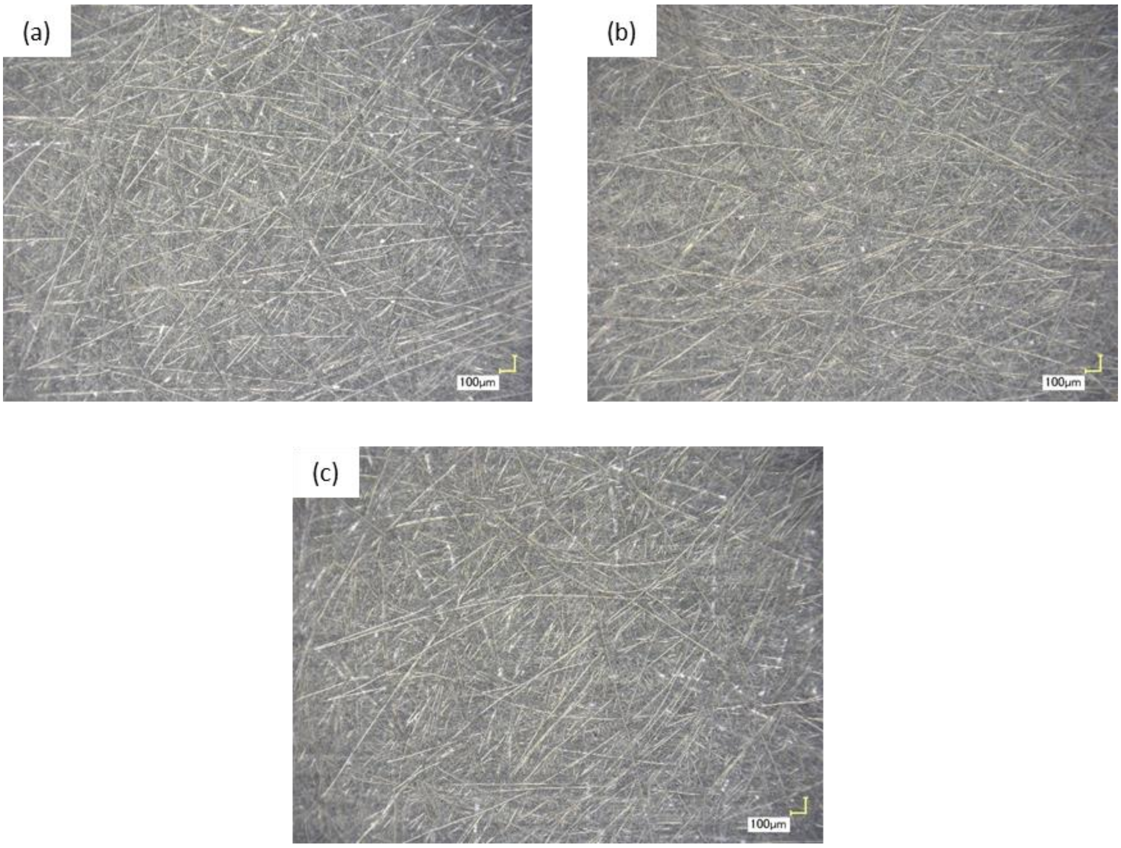


Figure 2-22 Microscope images of CPT(rCF/GF) under magnification of 100x: (a) GF: V_f 1%; (b) GF: V_f 2%; (c) GF: V_f 5%

2.4.3.3. Three point bending tests of CPT(rCF/GF)

Fig. 2-23 shows the flexural modulus of the experiments. There is no significant loss in rigidity of CPT(rCF/GF) materials based on the experiment results. The difference of the experiment results of CPT and of CPT(rCF/GF) materials is no more than 1%. Additionally, compared with CPT, the little increase of flexural modulus of CPT(rCF/GF1) and CPT(rCF/GF2) is probably caused by that longer and softer GF decreased the effect of linking weakest points in composites. However, the scatter of the experiment results are not significant, which is probably attributed to the number of specimens is not big enough to decrease the random errors during each experiment.

Based on the consideration of rule of mixture, the flexural modulus will be decreased by substituting the stronger fibers with weaker fibers. However, the results of CPT(rCF/GF) are not affected by the substitution of GF. The slight increase caused by small amount of GF can contrarily improve the flexural modulus.

Figure 2-24 shows the flexural strength of each kind of materials. CPT without contamination shows the highest flexural strength. CPT(rCF/GF5) shows the lowest flexural strength. Even though the existence of GF will decrease the strength of composite, but the similar results of CPT(rCF/GF1) and CPT(rCF/GF2) illustrate that a small amount of ductile GF hinders the failure propagation caused by CF. However, the V_f of GF increased to 5%, the weaker GF will affect the strength of composite more significantly.

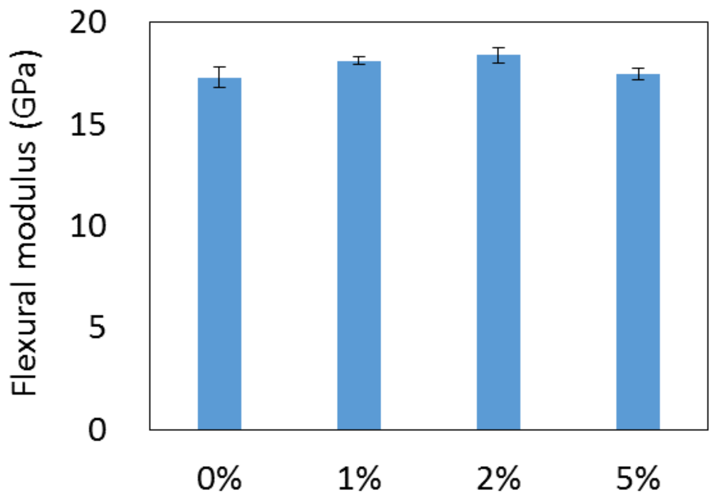


Figure 2-23 Results of flexural modulus of CPT(rCF/GF) materials

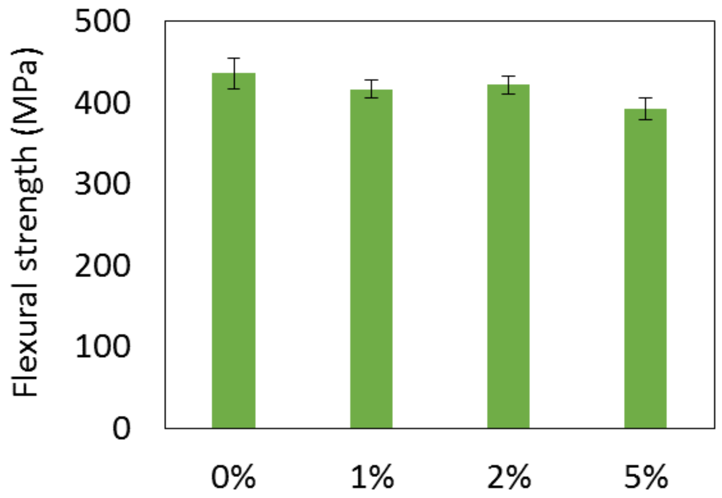


Figure 2-24 Results of flexural strength of CPT(rCF/GF) materials

2.4.3.4. Izod tests of CPT(rCF/GF)

Figure 2-25 shows the results of Izod tests. The impact energy absorption of CPT is 22.2 kJ/m^2 and that of CPT(rCF/GF5) is 19.6 kJ./m^2. The impact energy absorption of CPT is decreased by 12% when the 5% of V_f of GF is added. Even only 2% of GF is added to CPT materials, the impact energy absorption is largely decreased by 8%. The abnormal result of PT(rCF/GF1) is attributed to the lack of impregnation during molding, which means an small amount of voids in it will damage the potential of energy absorption.

However, there is only 4% loss of energy absorption of CPT(rCF/GF5) compared with CPt(rCF/GF2), which means the further additional GF will not further weaken the CPT(rCF/GF) materials by a same rate.

The ductile GF can delay the composite failure by connecting the cracks in matrix caused by the breakage of CF. This can also explain what happened in CPT(rCF/GF) during impact. During the impact, the additional energy can be absorbed by adding a small amount of GF, which bridged the weak points, such as fiber ends and micro-cracks in matrix. The connections in the composite improved the impact energy more randomly distributed throughout the specimen.

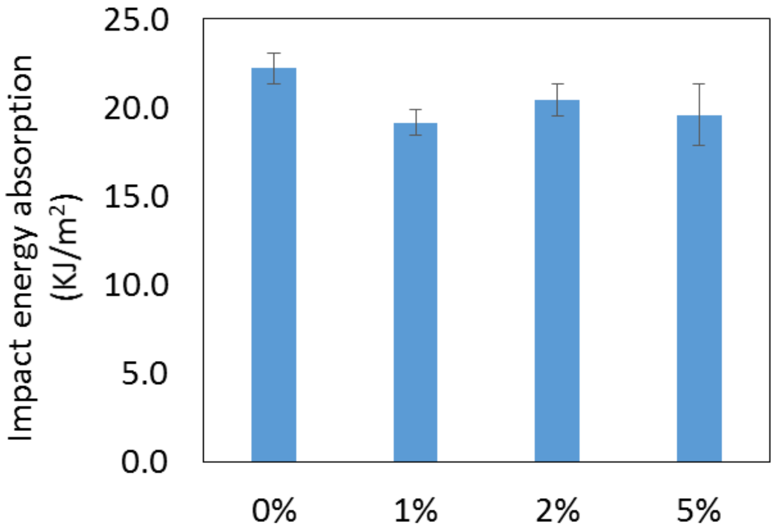


Figure 2-25 Results of impact energy absorption of CPT(rCF/GF) materials

Table 2-9 Results of three point bending tests of CPT(rCF/GF) materials

	V_f of GF	Flexural modulus (GPa)			Flexural strength (MPa)			failure strain (%)			Impact energy absorption (kJ/m^2)		
		Ave.	Stdv.s	CoV	Ave.	Stdv.s	CoV	Ave.	Stdv.s	CoV	Ave.	Stdv.s	CoV
CPT	0%	17.3	0.500	3%	436	18.900	4%	2.7	0.100	4%	22.2	0.860	4%
CPT-GF1	1%	18.1	0.187	1%	417	11.311	3%	2.5	0.051	2%	19.1	0.712	4%
CPT-GF2	2%	18.4	0.361	2%	422	10.889	3%	2.5	0.052	2%	20.4	0.898	4%
CPT-GF5	5%	17.5	0.258	1%	392	13.795	4%	2.5	0.139	5%	19.6	1.750	9%

2.5. Summary

i. Proper conditions of compression molding were investigated and kept through this research.

ii. A papermaking process was introduced to mix rCF with thermoplastic fibers. The basic mechanical properties were investigated, the CoV is small due to the uniformly dispersion of fibers.

iii. Mix-CPT were made to investigate the effect of mixed types of rCF. The variations of mechanical properties is according to the mechanical properties of constituents.

iv. CPT(rCF/GF) was investigated to discuss the effect of addition of different reinforcement fibers. The toughness of GF continuously contributes to the flexural modulus, which is no obvious in flexural strength and impact energy absorption.

Chapter 3. Reinforcement efficiency index – Factor Cs

3.1. Rule of mixture

3.1.1. Introduction of rule of mixture (RoM)

As acknowledged, rule of mixture (RoM) is a practically analytical approach to predict the mechanical properties of FRP. Even though this theory is composed for unidirectional FRP, a fitting coefficient describing the fiber architectures is normally used to predict the mechanical properties of randomly orientated fiber arrangement. There are two types of the fitting coefficient, one is empirical fitting factor and the other is based on analytical approach. Both are able to be used for specific FRP material systems. However, in actual analysis, the fitting coefficient is usually affected by the FOD, fiber length distribution (FLD) and other internal defects including fiber-fiber contact points, fiber ends and voids. Therefore, it is not clear enough as an instructive factor for rCFRTP manufacturing developments.

Composite materials have their microstructure designed in terms of their macroscopic constituents, e.g. fibers in a homogeneous matrix material. By controlling the choice of fibers, their volume fraction, and alignment, the mechanical properties may be tailored to meet specific design requirements.

In Figure 3-1, the diagram (a) shows a ‘uniaxial fiber-reinforced’ composite material, and (b) shows how the stress on the composite is carried by the fibers and the matrix. In normal situations, the fibers has a larger Young’s modulus than the matrix, and for the continuous fibers shown, where the strain is the same in the matrix and the fiber, the fiber stress is higher than the matrix stress. The Young’s modulus and the tensile strength of the composite are given by the ‘rule of mixtures’, as shown in Eqns. 3.1 and 3.2. The elastic modulus along the fiber direction can be controlled by selecting the volume fraction of the fibers.

The assumptions for rule of mixture are the constituent volume fraction in the RVE are assumed to be the same as those in the actual composite. The interface between fibers and matrix resin is perfectly bonded. The fiber and matrix materials are assumed to be linearly elastic and homogeneous.

$$E_c = E_f V_f + E_m V_m \tag{3.1}$$

$$\sigma_c = \sigma_f V_f + E_m \varepsilon_c V_m \tag{3.2}$$

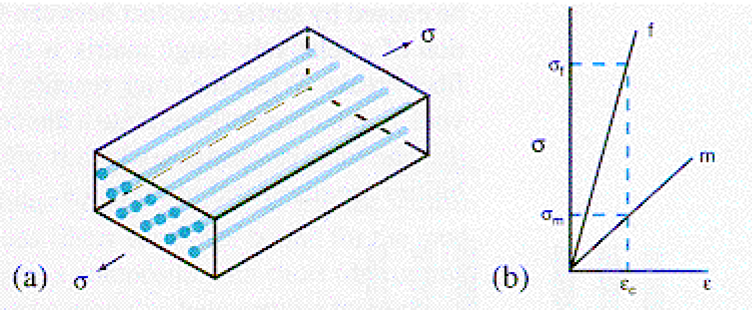


Figure 3-1 McMahon and Graham, "The Bicycle and the Walkman", Merion (1992)

3.1.2. Modified rule of mixture (MRoM) for mat-structural composites

In this research, an empirical fitting coefficient, Factor C_1 for modulus and C_2 for strength, of a modified rule of mixture (MRoM) , as shown in Eqns. 3.3 and 3.4. A papermaking process and a carding process were individually used to prepare two types of materials. One is called as carbon fiber paper reinforced thermoplastics (CPT) and the other is called as carbon fiber card web reinforced thermoplastics (CWT). The experimental results of flexural modulus and strength will be used to determine the Factor C_1 and C_2.

$$E_c = C_1 E_f V_f + E_m V_m \tag{3.3}$$

$$\sigma_c = C_2 \sigma_f V_f + E_m \varepsilon_c V_m \tag{3.4}$$

The reinforcement efficiency factor will be affected by: fiber orientation distribution (FOD), fiber length distribution (FLD) and internal defects (void content, fiber ends and fiber-fiber contact points). However, we need one parameter to inclusively describe the mentioned factors.

The rule of mixture is necessary to be modified for misaligned fiber oriented composites. Factor C_1 and C_2 are introduced for misaligned fiber reinforced composites. They are assumed that they are only affected by FOD, FLD and internal defects. Based on the composition of the equations, the effect of fiber type is also erased. Furthermore, Factor C_1 and C_2 are empirical parameters, which are calculated from experiment data.

However, there are limitations of these equations, which will affect the results calculated from them. Different from the conventional approach, MRoM is used to predict the mechanical properties of composites, the value of E_f and E_m are based on the measured mechanical properties from the real component materials.

In this research, the purpose is to provide a possible approach for industries with a guideline for them to develop their own mat-structural composites. Additionally, the V_f and V_m in the equations must be measured based on ash tests. However, the results from ash tests will be affected by the residual or over burn on the component materials. Therefore, the volume fraction of components are not as accurate as reality.

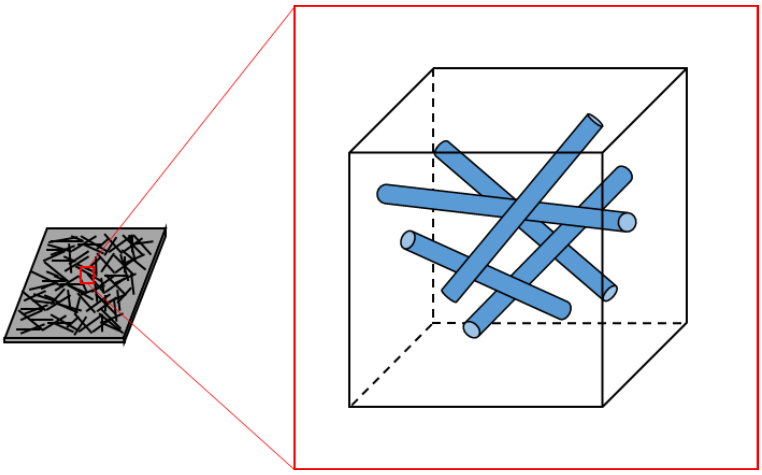


Figure 3-2 A representative volume element (RVE) of mat structured composites

3.2. Reinforcement efficiency index – Factor Cs

3.2.1. Definition of Factor Cs

In order to illustrate the value of Factor Cs, mix-CPT materials and CPT(rCF/GF) materials are investigated to calculate the correlated Factor Cs. Factor Cs are defined as an indicator for one composite material system, as shown in Figure 3-3. Therefore, no matter what the constituents are in the materials and what the contents are, there is only one Factor C for one composite material system. Based on this consideration, Eqns. 3.3 and 3.4 are modified as Eqns. 3.5 and 3.6.

$$C_1 = \frac{E_{c,exp} + E_m V_m}{\sum E_{fi} V_{fi}} \tag{3.5}$$

$$C_2 = \frac{\sigma_{c,exp} + E_m \varepsilon_{c,exp} V_m}{\sum \sigma_{fi} V_{fi}} \tag{3.6}$$

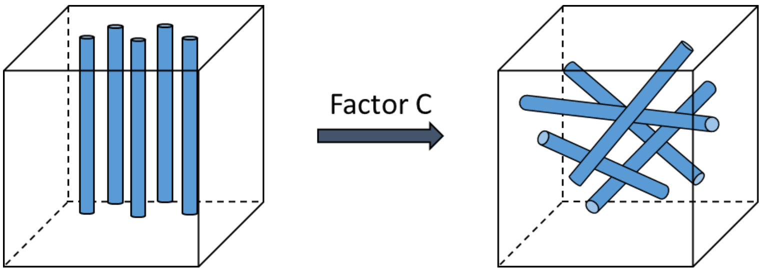


Figure 3-3 Consideration flow of introducing a reinforcement efficiency factor

3.3. Factor Cs of different combinations of reinforcement fibers

3.3.1. Factor Cs of mix-CPT

Calculated based on Eqns. 3.5 and 3.6, the Factor Cs of mix-CPT are shown in Figure 3-4.

Different from the results shown in Figures 2-18 and 2-19, increasing the V_f ratio of R-T800 will decrease the reinforcement efficiency in CPT materials. In Figures. 2-18 and 2-19, the flexural modulus and strength both increased when the V_f ratio of R-T800 fibers increased. However, the increasing trend of flexural modulus is much smaller than that of flexural strength. Because the difference of tensile modulus of R-T300 fibers and of R-T800 fibers is much smaller than the difference of tensile strength.

On the contrary, the Factor C_1 and C_2 calculated by Eqns. 3.5 and 3.6 are shown in Figure 3-4. Both the Factor C_1 and C_2 will decrease when the V_f ratio of R-T800 fibers increased. The slopes of both trend lines are similar with each other.

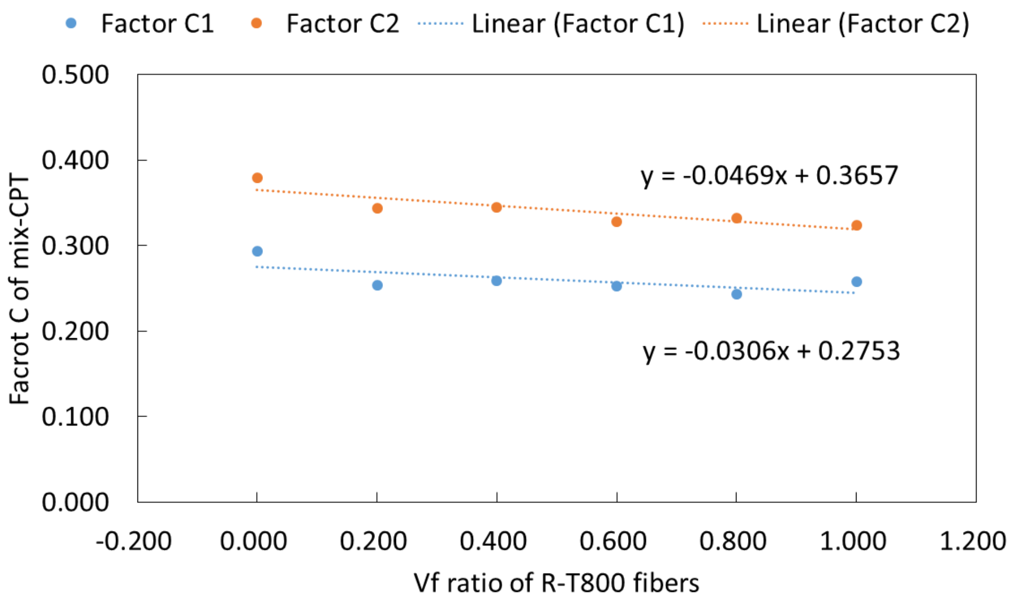


Figure 3-4 Factor Cs of mix-CPT materials

3.3.2. Factor Cs of CPT(rCF/GF)

Figures 2-23 and 2-24 show the results of flexural modulus and of flexural strength of CPT(rCF/GF) materials, the change trends are different from each other. The total V_f of CF and Gf is constant of 20%. When the V_f of Gf increased from 0% to 1%, the flexural modulus of CPT(rCF/GF) increased accordingly. Even though the tensile modulus of GF is much smaller than CF, the isotropic properties of GF release the stress concentrations around fiber-fiber contact points. However, when the V_f of GF reached 5%, the alleviating effect cannot resist the negative effect from the increasing content of weaker constituent. The alleviating effect by adding GF also exists in flexural strength but the flexural strength will decrease even only 1% of GF are added into CPT materials. Therefore, the reinforcement efficiency of CPT(rCF/GF) materials cannot be clearly illustrated because of alleviating effect.

The results of Factor Cs calculated by Eqns. 3.5 and 3.6 are shown in Figure 3-5. The change trends of Factor C_1 and C_2 are similar with each other. It can be confirmed by the slopes in Figure 3-5 that the change trends of Factor C_1 and C_2 are similar. When the content of GF increased, the reinforcement efficiency both in flexural modulus and flexural strength will increase.

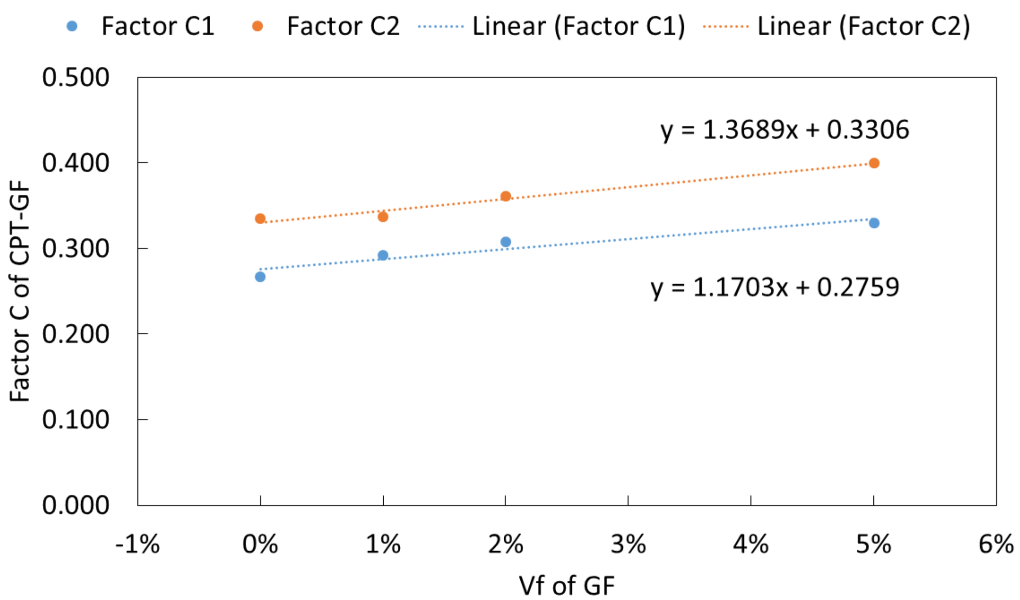


Figure 3-5 Factor Cs of CPT(rCF/GF)

3.4. Factor Cs of mat-structural composites made by different fabricating methods

3.4.1. A carding process

3.4.1.1. Review of carding process

Carding is a mechanical process that disentangles, cleans and intermixes fibers to produce a continuous web or sliver suitable for subsequent processing. This is achieved by passing the fibers between differentially moving surfaces covered by card clothing [1]. Figure 3-6 shows a carding machine.

In this study, a carding process was introduced to fabricate the rCF and the matrix resin fibers. The carding machine is composed by the needles of interactive perpendicular movements with a belt of unidirectional movement. The cooperative movements of the components of a carding machine make the resultant mat structural materials containing the CF aligned along the belt movement direction. The fabricated mat materials are called carbon fiber card web reinforced thermoplastics (CWT).

As shown in Fig. 3-7, the CF and the matrix resin fibers are directly added into a carding process and then the mixture will be fabricated into CWT sheet by the carding process. Due to the processing characteristics of the carding process, the direction of the belt moving direction is termed as L-direction and the perpendicular direction is termed as T-direction.

The mechanical properties are believed to be different on L-direction and on T-direction.

Figure 3-6 A photo of carding machine

3.4.1.2. CWT preforms

CWT preforms are prepared by carding process. Figure 3-7 shows a schematic image of the carding process. In this process, PA6 fibers and RCF are directly fed into a carding machine. After the associative movements of the needles and of the belt, continuous CWT preforms will be rolled automatically for package.

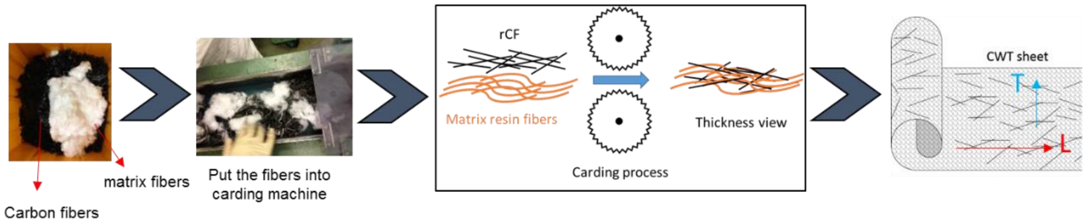


Figure 3-7 A flowchart description of a carding process

3.4.2. Mechanical properties of CWT

3.4.2.1. Materials and compression molding conditions

In order to avoid negative influence of CF degradation on the mechanical properties of CWT, TORAYCA®T700S fresh carbon fiber and polyamide (PA) fibers were used in fabricating preforms. CWT preforms with 20%, 30% and 40% of V_f were manufactured initially by carding process.

In order to clearly identify specific CWT material of specific V_f and of specific stacking method (unidirectional, cross stacking, stretched and etc.), we term the CWT materials as shown in Figure 3-8. The character on the left of "CWT" means the stacking method, "C" means cross-plied CWT preforms and "S" means stretched CWT preforms (S-CWT will be introduced later). If there is no character on the left, it means the CWT preforms are unidirectionaly overlapped. The number on the right of "CWT" means the target V_f. The real V_f will be examined through ash tests.

The fabricated CWT preforms of different target V_f are shown in Figure 3-9.

The molding pressure for CWT20 and CWT30 is 7 MPa and that for CWT40 is 9 MPa. Different from CPT materials, in which the average fiber length is around 6 mm, the largest fiber length in CWT materials is as long as 12 cm. The choice of longer CF is due to the rough carding process, which will significantly decrease the fiber length. Longer fiber of 12 cm can ensure the fibers after carding to maintain the fiber length over than critical length. The longer the fiber is, the more complex internal micro-structures will be. The longer fibers in CWT materials will be curved by intermingling with each other and with PA fibers after carding process. The complex internal micro-structures will hinder the quality of impregnating process. When the V_f is over than 40%, the additional fiber content will induce the decreased fiber-fiber distance, which will further increase the difficulty of resin impregnating. Therefore, the molding pressure for CWT materials is higher than that for CPT materials.

The molding temperature is 270 ℃, because the melting point of matrix resin is 250 ℃ and plus 20 ℃ is for temperature difference in the mold.

C/S-CWT20

C/S	CWT	20
None: Unidirectional stacking ***C***: cross plied stacking ***S***: stretched preforms	CFRTP term (based on carding process)	Fabricating parameter index (based on target V_f)

Figure 3-8 Terminological method

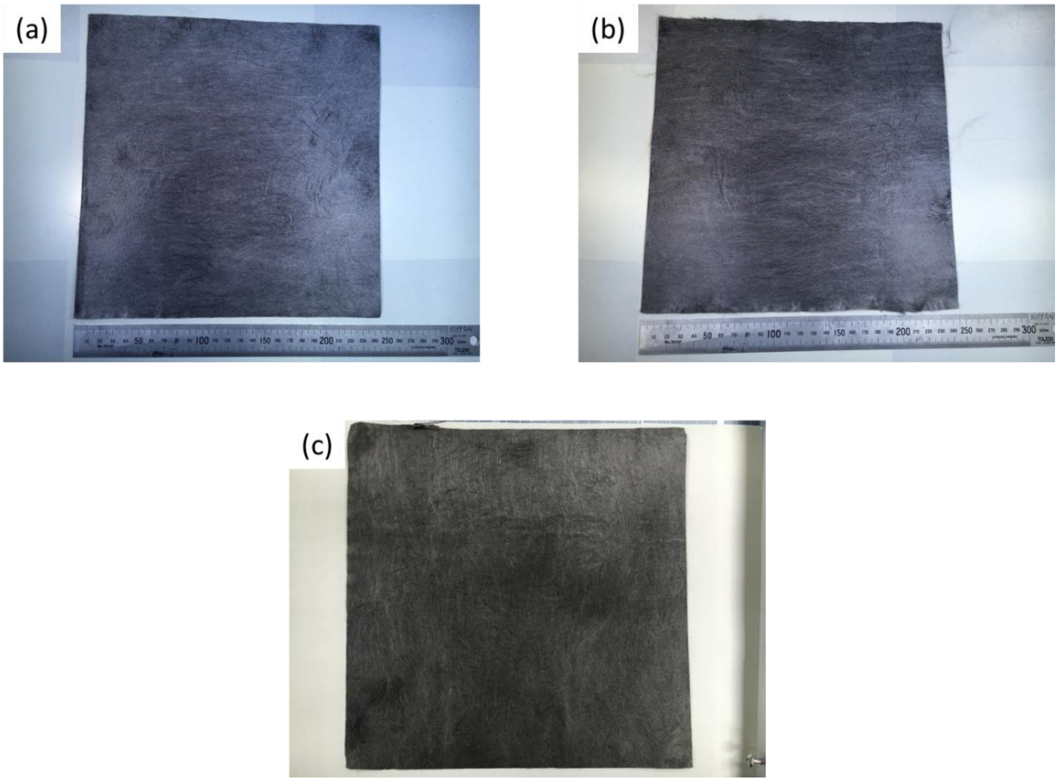


Figure 3-9 CWT preforms before molding: (a) CWT20; (b) CWT30; (c) CWT40

3.3.2.2. Ash tests

The results of ash tests are listed in Table 3.1.

Table 3-1 Types of CWT with different V_f

Materials	CWT20	CWT30	CWT40
Molding pressure (MPa)	7	7	9
V_f (%)	29.9	30.6	42.4
V_v (%)	1.9	0.9	5.6

3.3.2.3. Three point bending tests

Flexural properties of CWT were measured by three point bending test according to JIS K 7074 with universal testing machine (AUTOGRAPH AGS-X 5KN, Shimadzu Co.). As in the tensile tests, five specimens were prepared in each direction. The size of specimen is 50 mm in length, 10 min in width and 2 mm in thickness. The span of the supporters on the testing machine is determined by the thickness of the specimens with the span-to-thickness ratio of 16:1 and the crosshead speed is 1mm/min.

As shown in Figure 3-10, the flexural modulus of CWT materials in L-direction will be increased when the V_f of CWT increased. However, the real V_f of CWT20 almost reached 30%, as shown in Table 3-1, the flexural modulus of CWT20 is similar with that of CWT30. It shows highest flexural modulus when the V_f of CWT is 40%. Different from the L-direction, T-direction shows small variations in flexural modulus.

Different from the results of flexural modulus, the variance of flexural strength among different V_f of CWT materials is much smaller than flexural modulus, as shown in Figure 3-11. Because the elastic modulus is mainly due to the properties and the V_f of the constituents and the elastic strength will be additionally affected by internal defects. Internal defects include void content, fiber-fiber contact points, fiber ends.

The results of ash tests listed in Table 3-1 illustrate that the volume fraction of CWT materials is over than 40%, the void content is 5.6%, which is almost five times of the void content of CWT30. The voids in composite materials will induce stress concentrations that will cause cracks when the materials are bearing loads.

In actual applications of materials, fabricated CFRTP preforms will be overlapped as cross plies because overlapped stacking method can maintain the resultant products with good quasi-isotropic, which can enhance the design flexibility of products.

The results of three point bending tests of cross plied CWT30 materials are shown in Figures 3-12 and 3-13. Both the flexural modulus and flexural strength of C-CWT30 are in the middle of those of CWT30 in L-direction and in T direction. Furthermore, the coefficient of variation (CoV) of flexural strength is small enough, which means CWT materials show good stability of mechanical properties.

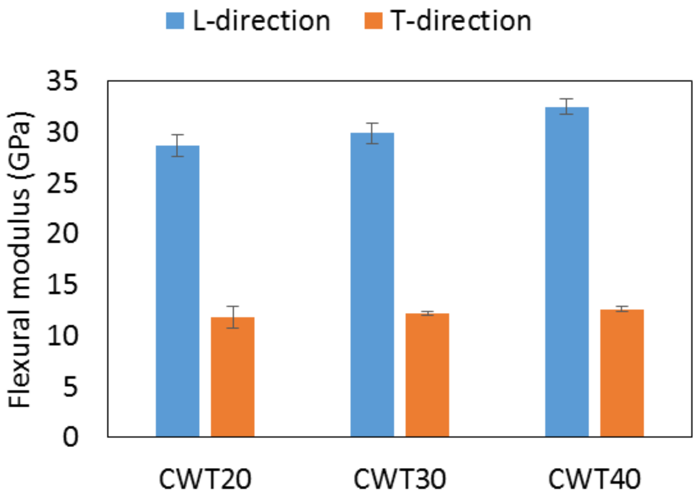


Figure 3-10 Results of flexural modulus of CWT materials

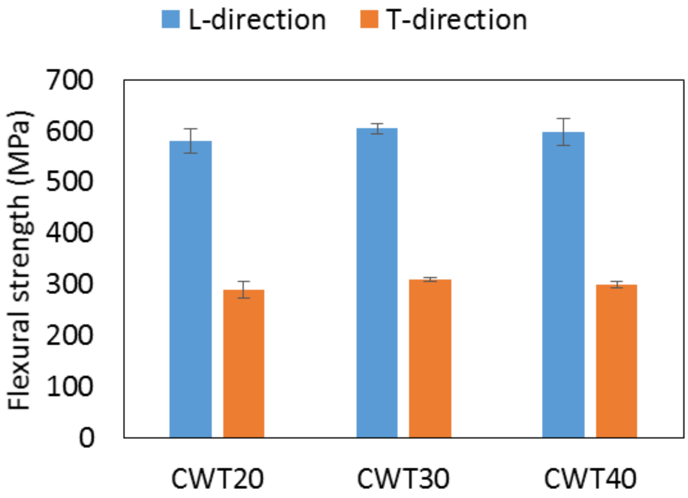


Figure 3-11 Results of flexural strength of CWT materials

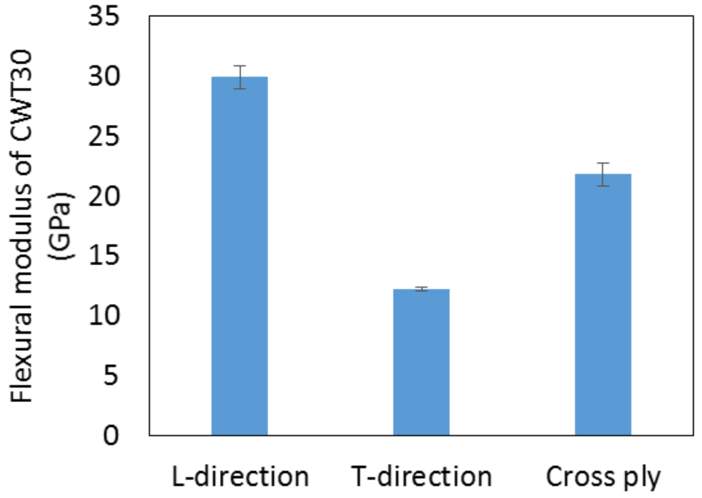


Figure 3-12 Results of flexural modulus of CWT30 of different stacking methods

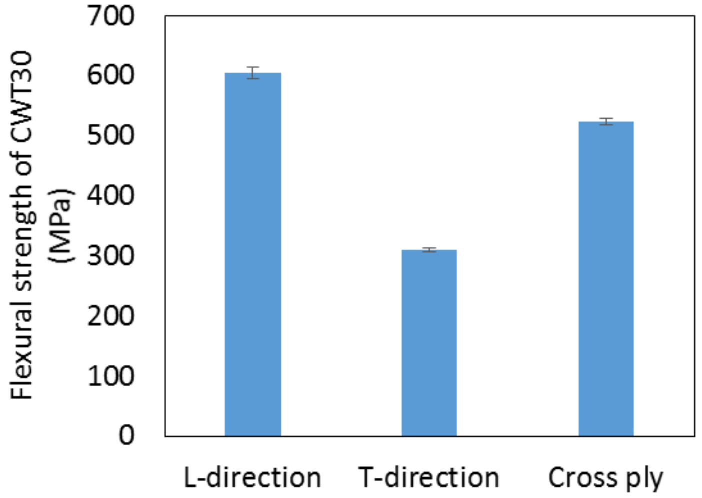


Figure 3-13 Results of flexural strength of CWT30 of different stacking methods

Table 3-2 The mechanical properties of CWT materials

Material item	V_f	Vv	Stacking method			Flexural modulus (GPa)			Flexural strength (MPa)		
			L-direction	T-direction	Cross ply	Ave	Stdv.s	CoV	Ave	Stdv.s	CoV
CWT20	29.90%	1.85%	✓			28.7	1.042	4%	581	23.857	4%
				✓		11.8	1.013	9%	290	15.418	5%
CWT30	30.60%	0.90%	✓			29.9	0.999	3%	604	9.504	2%
				✓		12.2	0.166	1%	310	3.464	1%
CWT40	42.40%	5.55%	✓			32.5	0.810	2%	598	26.500	4%
				✓		12.6	0.273	2%	299	6.309	2%
C-CWT30	31.30%	1.92%			✓	21.8	0.933	4%	523	5.860	1%

3.5. Discussion of how to use Factor Cs

3.4.1. Conventional investigation approaches

3.4.1.1. Comparing mechanical properties based on mechanical properties

As shown in Figures. 3-14 and 3-15, the flexural modulus and flexural strength are affected by the V_f of fibers. Compared with mix-CPT materials, the V_f of CWT Vf29.9% has additional 50% V_f but the flexural modulus increased with 85%. This is contributed by the difference of FOD in mix-CPT and CWT materials. However the flexural strength is only increased with 61% comparing CWT V_f 29.9% with mix-CPT materials. Void content makes the mechanical properties of CWT materials lose the fitting ability with rule of mixture. The void content of CWT V_f 42.4% reaches 5.6%, which is not small enough to be accepted by industries. However, the actual V_f has reached 40%.

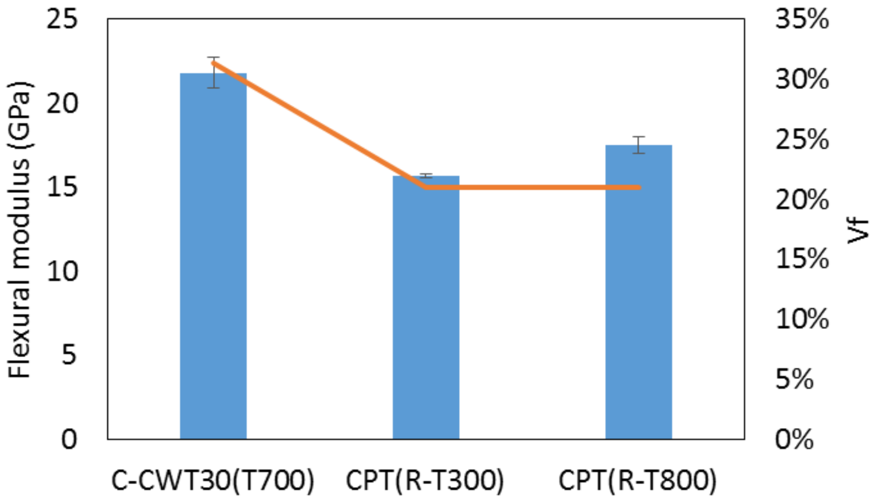


Figure 3-14 Results of flexural modulus of CWT and CPT materials with correlative V_f

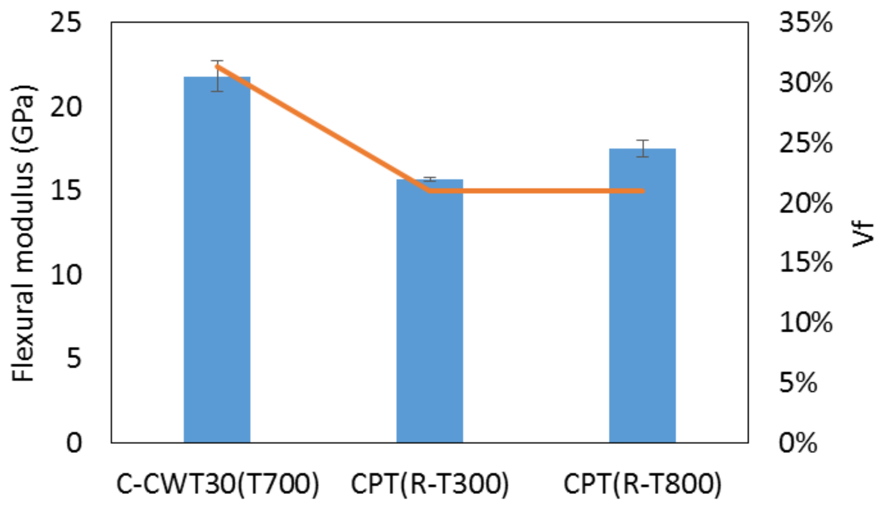


Figure 3-15 Results of flexural strength of CWT and CPT materials

3.4.1.2. Comparing mechanical properties based on normalized mechanical properties

Different from the direct compare based on the mechanical properties, the mechanical properties can be varied by V_f. Same type of CFRTP materials, the mechanical properties will increase with the increase of the V_f. Therefore, normalized mechanical properties are used to compare the reinforcement efficiency of the materials. Normalized mechanical properties are derived by dividing the mechanical properties with real V_f. As shown in Figures 3-16 and 3-17.

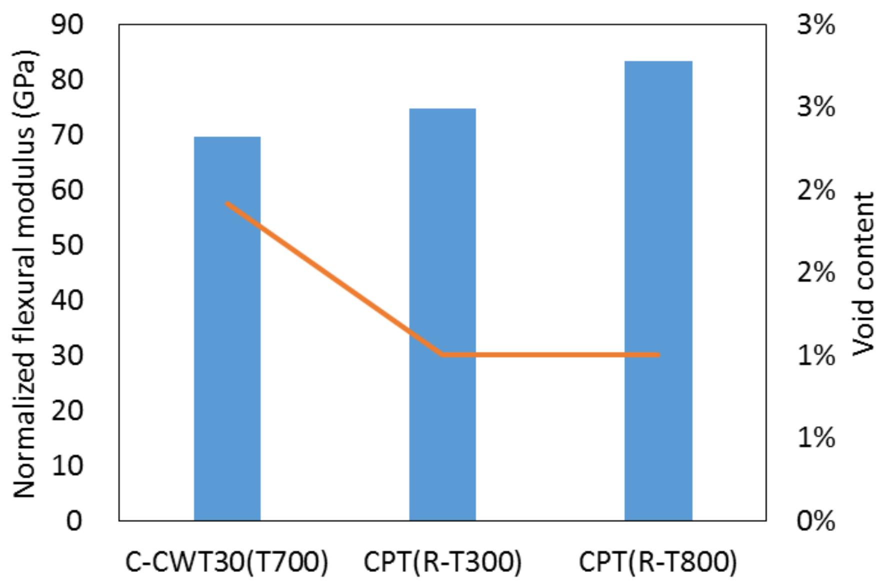


Figure 3-16 Normalized flexural modulus of CWT and CPT materials

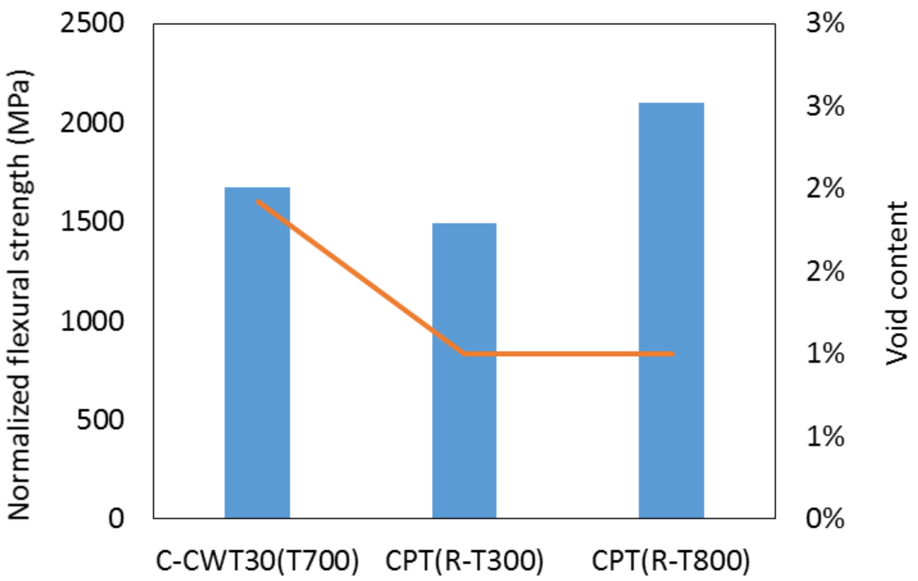


Figure 3-17 Normalized flexural strength of CWT and CPT materials

3.4.2. A novel propose of investigation approach based on Factor Cs

Even though normalized mechanical properties are enough to compare the performance potential of the materials made by same manufacturing methods, it is still difficult and controversial to use them to compare the mechanical performance of materials made by different manufacturing methods. Therefore, a more independent value from internal defects is more necessary. Derived from Eqns. 3.3 and 3.4, Factor C_1 and C_2 illustrate the reinforcement efficiency on flexural modulus and on flexural strength respectively can be calculated by Eqns. 3.7 and 3.8.

$$C_1 = \frac{E_{c,exp} + E_m V_m}{E_f V_f} \tag{3.7}$$

$$C_2 = \frac{\sigma_{c,exp} + E_m \varepsilon_{c,exp} V_m}{\sigma_f V_f} \tag{3.8}$$

Where, $E_{c,exp}$ and $\sigma_{c,exp}$ are the flexural modulus and flexural strength from three point bending tests, E_f and E_m are the tensile modulus of fibers and of matrix resin respectively, V_f and Vr are the volume fraction of CF and of matrix resin, and ε_c is the failure strain from three point bending tests. The basic properties of the constituents of CPT and CWT materials necessary for E.

From the MRoM, the predictions of mechanical properties of composites can be conducted through the mechanical properties and V_f of the components. The former information can be acquired from the database of individual research center and from the internet, which is more easily accessed. The latter information is designable information based on the development considerations. There are several types of information need to be considered when a new material is designed.

This research is mainly focused on how to guide the industries to develop discontinuous carbon fibers reinforced thermoplastics, especially develop materials with rCF. The discontinuous fiber length distribution and random fiber orientation distribution are interference information to discourage the industry to use rCF. Therefore, an index is necessary to discuss the potential mechanical properties of rCFRTP made by different manufacturing processes.

Traditional investigation approaches based on mechanical experiments will increase the cost of development. Because if we want to change the components or the FOD and FLD of the reinforcement fibers, we have to prepare enough preforms to make plates for mechanical experiments, which need a large amount of the specimens of specific size. However, each step of one development project needs a very little change, repeating the standard mechanical investigations will increase the costs in time and in labor. Therefore, longer development circle will discourage the passion to develop more potential materials, especially during the development of remanufacturing rCF. Therefore, if we can confirm the Factor Cs of specific manufacturing process and of specific internal structure, we can predict the reinforcement efficiency based on much fewer mechanical expeirmens.

In later sections, the Factor Cs will be used to compare the discontinuous CFRTP materials based on different V_f of same material systems and on same V_f of different manufacturing processes.

3.4.2.1. *Comparing reinforcement efficiency based on Factor Cs*

The calculated results are shown in Figure 3-18. Compared the Factor Cs in Figure 3-18 with the normalized mechanical properties shown in Figures 3-16 and 3-17. The reinforcement efficiencies both in flexural modulus and in flexural strength are highest although the normalized flexural properties are highest in CPT reinforced by R-T800 fibers. The normalized flexural properties are strongly affected by the mechanical properties of the components. However, after removing the effect of the mechanical properties of components, the reinforcement efficiency are different.

As shown in Figure 3-18, C-CWT30, CPT(R-T300) and CPT(R-T800) are similar mat-structural composite materials and all of them are reinforced by discontinuous CF. Therefore, Factor C_1 of all materials are closed to each other. Because flexural modulus are mainly affected by the internal component arrangements. Different from elastic modulus, the flexural strength will be additionally affected by internal defects including void content, fiber-fiber contact points and fiber ends. The V_f of CPT materials are both 20% and the number averaged fiber length is around 6 mm. The difference of fiber diameter of R-T300 and R-T800 fibers makes the number of fiber ends different from each other. The smaller diameter of R-T800 introduced more fiber ends in CPT materials. Therefore, the reinforcement efficiency for CPT(R-T800) decreased by additional fiber ends compared by CPT(R-T300).

Different from CPT materials, the number average fiber length in CWT is around 120 mm, which cause fiber curves and more distributed fiber length. Therefore, the reinforcement efficiency for flexural strength is weaker in C-CWT30.

Table 3-3 The basic properties of the component materials

	ρ (g/cm^3)	E (GPa)	σ (MPa)	ε_f (%)
T300	1.760	230	3530	1.50
T800	1.800	294	5880	2.00
T700	1.800	230	4900	2.10
PA6	1.140	2.0	-	-
PA66	1.112	2.9	-	-

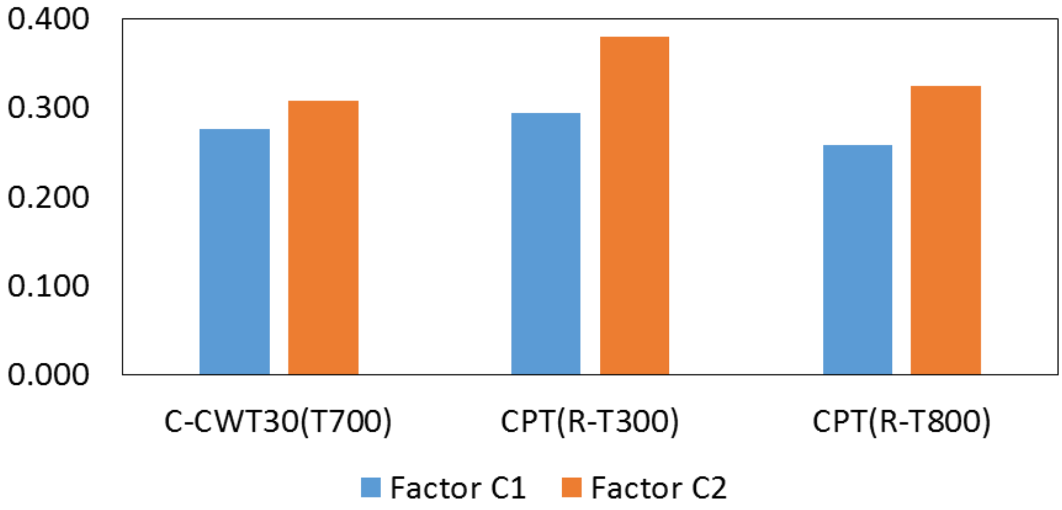


Figure 3-18 Compare the reinforcement efficiency based on Factor Cs

3.4.2.2. Factor Cs of one material system

After discussing the potential of Factor Cs, it is confirmed that the Factor Cs can be used for identifications of the reinforcement efficiency composed by the internal fiber architectures and fiber morphologies (e.g. FOD and FLD).

Figure 3-19 shows the Factor C_1 of CWT materials. After removing the effect of the V_f and the mechanical properties of the components, the reinforcement efficiency is stable when the V_f content is 20% and 30%. From the results of ash tests, the real V_f of CWT20 and CWT30 are closed to each other. The V_f of CWT40 can reach 40%, but the reinforcement efficiency is not good enough compared with CWT20 and CWT30. From the mechanical properties of CWT materials, the flexural modulus of CWT40 is 8.7% higher than that of CWT30 in L-direction. The coefficient of variation (CoV) of flexural modulus of CWT40 is similar to that of CWT30. Traditional compare based on mechanical properties is not enough to illustrate the real effect of different parameter groups.

After comparing the Factor C_1 for flexural modulus, as shown in Figure 3-20, the reinforcement efficiency CWT40 is not as promising as CWT20 and CWT30, although the fabricating parameters of CWT20 are closed to CWT30. The results of Factor C_1 in L-direction illustrate that the reinforcement efficiency based on fabricating process can be stable both in CWT20 and in CWT30. However, the low reinforcement efficiency of CWT40 will make the cost-benefit of current fabricating parameters to make CWT40 questionable. If we want to improve the reinforcement efficiency therefore to improve the cost-benefit of CWT40, the fabricating parameters must be modified furthermore.

The similar Factor C_1 and C_2 of CWT20 and CWT30 make the real V_f of CWT20 is 29.9% and that of CWT30 is 30.6%. The almost same real V_f make the CWT20 is unnecessary in CWT material system based on the consideration of cost-benefit. Therefore, the fabricating process can be modified for CWT20 to decrease the correlated time and labor cost.

In this thesis, the fiber length distribution (FLD) of the CF in CWT is similar for CWT20, CWT30 and CWt40. Therefore, after carding process, the FLD of three types of CWT materials will be constant, which can be confirmed by the Factor C_1 and C_2 both on L-direction and on T-direction. The change trends of Factor C_1 and of Factor C_2 are same.

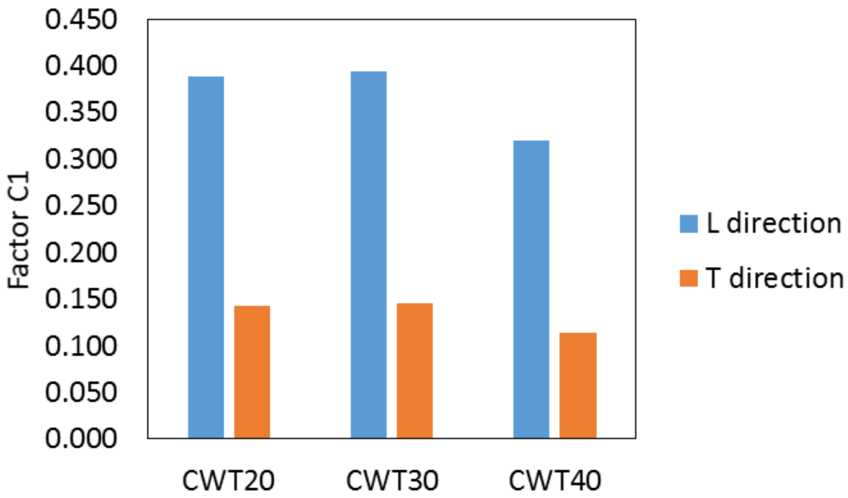


Figure 3-19 Factor C_1 of different CWT materials

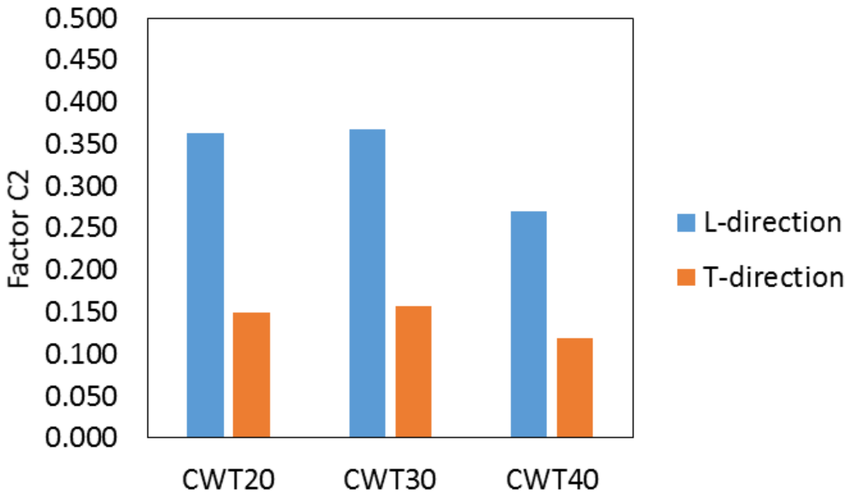


Figure 3-20 Factor C_2 of different materials

3.5 Determination of quality of alignment process based on Factor Cs

3.5.1. Stretched CWT materials

Based on the characteristics of the carding process, CF can be aligned after the CWT sheet is stretched.

Based on the characteristics of carding process, a fabricating process for non-woven mat materials, the carbon fibers can be distributed during the resin fibers being fabricated by the movement of the needle drums. Different from the papermaking process, the carding process don't need water as a distribution agent, therefore, there will be no drying step for the CWT materials, which make the development circle shorter.

However, in order to further develop the manufacturing of rCF, the alignment process is critical process to re-manufacturing rCFRTP. In this thesis, the CWT materials will be stretched by hands with a stretch ratio defined by Eqn. 3.9. The stretch process, alignment process of CWT fabricating process, is shown in Figure 3-21. After stretching, the discontinuous CF will be aligned along with stretching the non-woven web of resin fibers. Therefore, it is predicted that the fiber orientations will be more closed to L-direction. The more concentrated fiber orientations will improve the FOD of rCF in furture.

$$Stretch\,ratio = \frac{L' - L}{L} \cdot 100\% \tag{3.9}$$

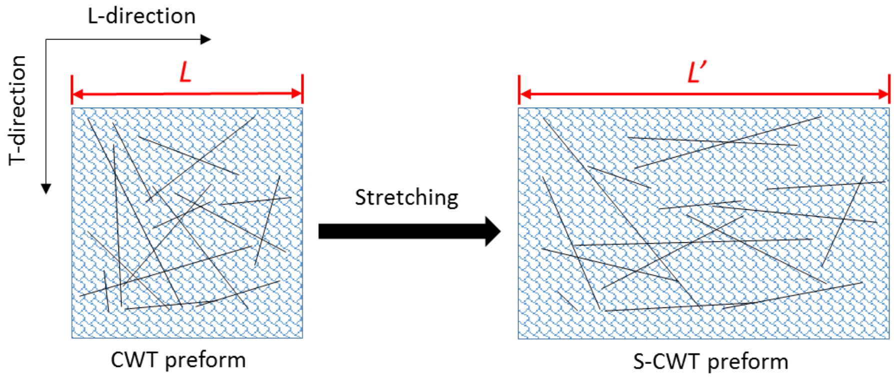


Figure 3-21 A schematic image of stretching CWT preforms

3.5.1.1. Factor Cs of non-stretched and stretched CWT materials

As discussed in 3.4.1, conventional investigation of mechanical potential of materials is time and labor consuming. In conventional investigation, the materials of each development step must be prepared with patience. The amount of materials have to be enough for molding and for all mechanical experiments including tensile tests, three point bending tests, impact tests and etc. The complicated investigation approaches will make the development duration too long. Additionally, the mechanical properties must be analyzed by thorough considerations of several critical angles: the mechanical properties and V_f of components, FOD, FLD and internal defects. The conclusion derived from the conventional compare is not suitable to compare with other kind materials. Therefore, Factor Cs, the fitting coefficients for modified rule of mixture (MRoM), are more suitable to analyze the improvement of fabricating process.

Figures 3-22 and 3-23 shows the Factor Cs of non-stretched and stretched CWT30 materials. The Factor C_1 of S-CWT30 is 0.498 and that of CWT30 is 0.394. The increase ratio is 26.4%. The Factor C_2 of S-CWT30 is 0.515 and that of CWT30 is 0.515. The increase ratio is as high as 40.3%. Figures 3-24 and 3-25 show the Factor Cs of non-stretched and stretched CWT40 materials. The Factor C_1 of S-CWT40 is 0.404 and that of CWT40 is 0.320. The increase ratio is 26.3%. The Factor C_2 of S-CWT40 is 0.363 and that of CWT40 is 0.270. The increase ratio is 34.4%.

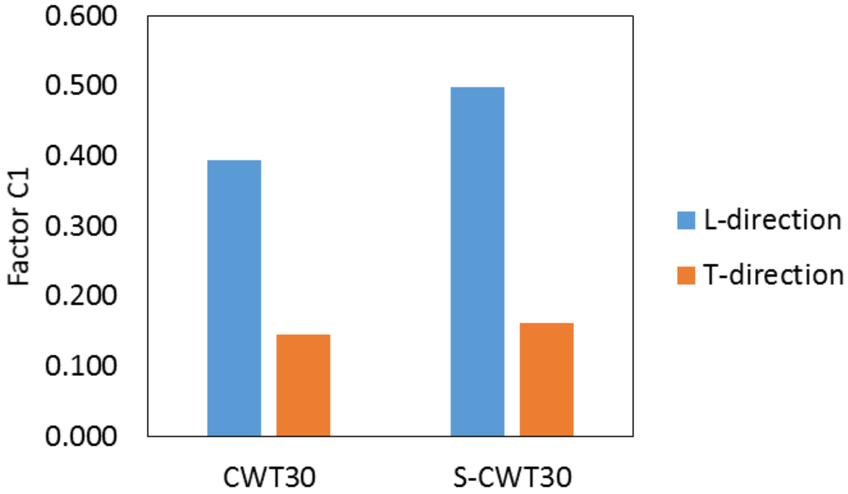


Figure 3-22 Factor C_1 of non-stretched and stretched CWT30 materials

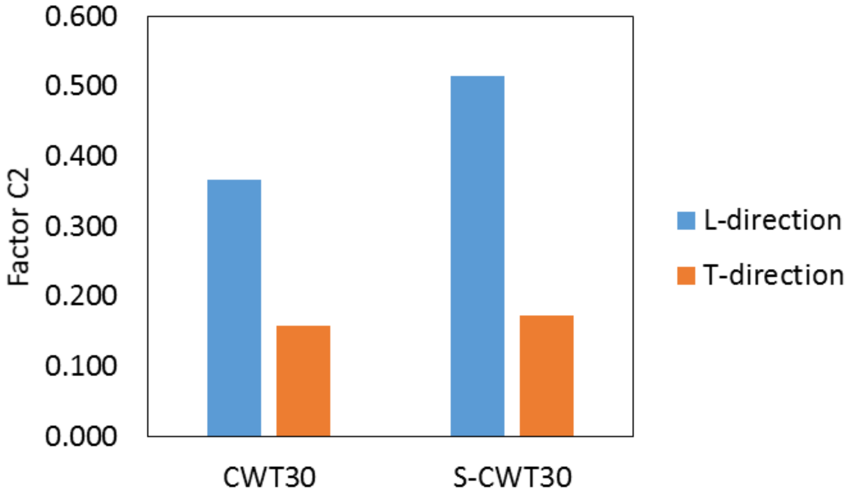


Figure 3-23 Factor C_2 of non-stretched and stretched CWT30 materials

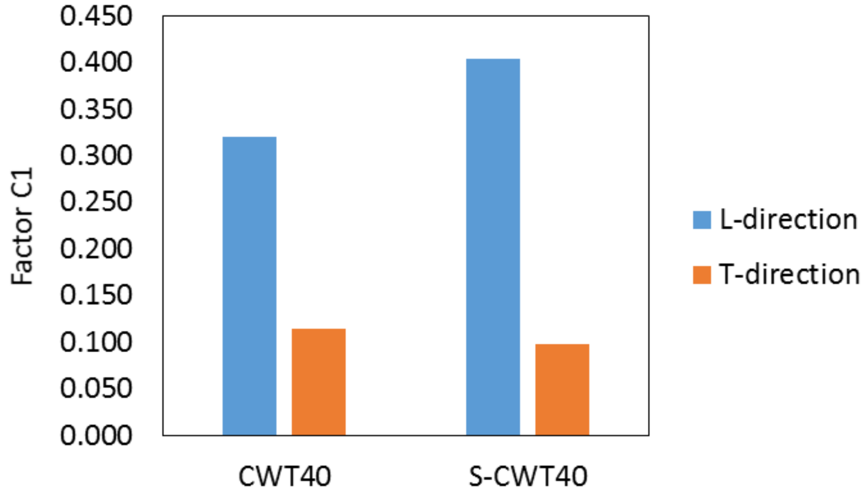


Figure 3-24 Factor C_1 of non-stretched and stretched CWT40 materials

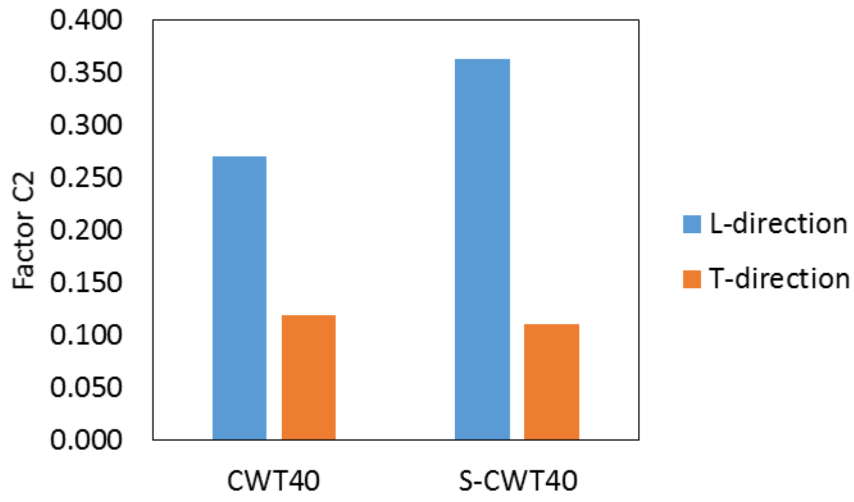


Figure 3-25 Factor C_2 of non-stretched and stretched CWT40 materials

3.5.1.2. Relation between stretch ratio and Factor Cs

Figure 3-26 shows the relation between stretch ratio and improvement of Factor Cs. The stretch ratio of CWT30 is 30% and that of CWT40 is 68%. The reinforcement efficiency in flexural modulus will be improved by almost 26% under both stretch ratio. Therefore, the reinforcement efficiency in this study will not be further improved by stretching the preforms more. The reinforcement efficiency is improved by stretching preforms. However, stretching preforms of CWT40 by the stretch ratio of 68% cannot improve the reinforcement efficiency more than stretching preforms of CWT30 by stretch ratio of 30%. The decreased improvement of Factor Cs of CWT40 is mainly due to the void content, which is as high as 5.6%. The current fabricating parameters for CWT40 preforms are not good enough. The void content is the critical problem to be solved in future if higher than 40% of fiber content is required.

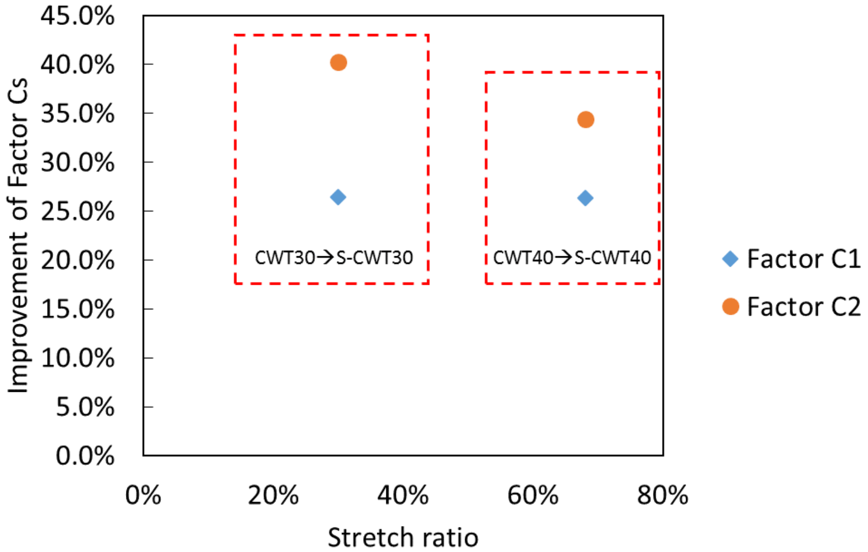


Figure 3-26 The relation between stretch ratio and improvement of Factor Cs

Table 3-4 The Basic information of CWT materials

	Stretch ratio	V_f	Vv	L-directon	T-direction	QI	Flexural modulus (GPa)	Flexural strength (MPa)	Factor C_1	Factor C_2
CPT(R-T300) Mix-CPT(1.0/0.0)	-	21%	1%			✓	16	313.9	0.293	0.380
Mix-CPT(0.8/0.2)	-	21%	1%			✓	15	322.3	0.254	0.344
Mix-CPT(0.6/0.4)	-	21%	1%			✓	15	360.0	0.259	0.345
Mix-CPT(0.4/0.6)	-	21%	1%			✓	16	379.7	0.252	0.328
Mix-CPT(0.2/0.8)	-	21%	1%			✓	16	415.3	0.243	0.333
CPT(R-T800) Mix-CPT(0.0/1.0)	-	20%	1%			✓	18	441.1	0.258	0.324
CPT(rCF/GF1)	-	19%+1%	1%			✓	18	416.6	0.292	0.337
CPT(rCF/GF2)	-	18%+2%	1%			✓	18	421.8	0.308	0.361
CPT(rCF/GF5)	-	15%+5%	1%			✓	17	392.1	0.330	0.399
CWT20	-	29.9%	2%	✓			29	580.8	0.389	0.363
					✓		12	289.9	0.143	0.149
CWT30	-	30.7%	1.7%	✓			30	604.3	0.394	0.367
					✓		12	310.0	0.145	0.158
CWT40	-	42.3%	5.6%	✓			33	597.9	0.320	0.270
					✓		13	298.8	0.114	0.118
C-CWT30	-	31.3%	1.9%			✓	22	523.0	0.276	0.307
S-CWT30	30%	29.3%	1.3%	✓			36	787.3	0.498	0.515
					✓		13	308.1	0.161	0.172
S-CWT40	68%	39.1%	5.5%	✓			37	731.0	0.404	0.363
					✓		10	268.6	0.098	0.111

3.5. A map of rCFRTP development composed by Factor Cs

3.5.1. How to build the development map

The discussion of how to determine the reinforcement efficiency based on the Factor Cs has been given in former sections. The Factor Cs are fitting coefficients of modified rule of mixture (MRoM). They can be used to compare the reinforcement efficiency contributed by fabricating process. The Factor Cs are not only contributed by the fabricating process but also by the FOD of the internal fiber architecture.

Based on the consideration of MRoM, the potential of mechanical properties of materials can be illustrated without the interference of the mechanical properties and V_f of the components. Deriving these factors, the reinforcement efficiency can be discussed only based on the internal fiber architectures including FOD and FLD.

In future of the rCFRTP development, it is critical step to improve the FOD by alignment process. In this chapter, an alignment process was introduced by stretching CWT preforms. Even though the stretching process in this study was conducted by hands, the FOD is thought to be inclined along the stretching direction.

FOD is one of the composition of Factor Cs so we can use them to identify the improvement quality of the stretching process. Additionally, the unidirectional material will be used in cross plied stacking method in actual applications. Factor Cs in flexural properties will be affected by stacking methods. Therefore, the Factor Cs of mechanical properties in quasi-isotropic is actually used for markets.

Therefore, the Factor Cs in both unidirectional and cross plied stacking methods need to be discussed simultaneously. In this chapter, we proposed a map to help industries to develop the discontinuous CFRTP materials.

The structure of the development map is shown in Figure 3-27. The X-axis is the Factor Cs of the mechanical properties on T-direction, which is the direction perpendicular to the main fiber orientation direction. The Y-axis is the Factor Cs of the mechanical properties on L-direction, which is the direction parallel to the main fiber orientation direction. The diagonal means the mechanical properties on L-direction is as same as on T-direction, therefore it can illustrate the Factor Cs of quasi-isotropic stacking method. If we put the Factor Cs of all materials on this map, we can clearly know the potential of specific materials.

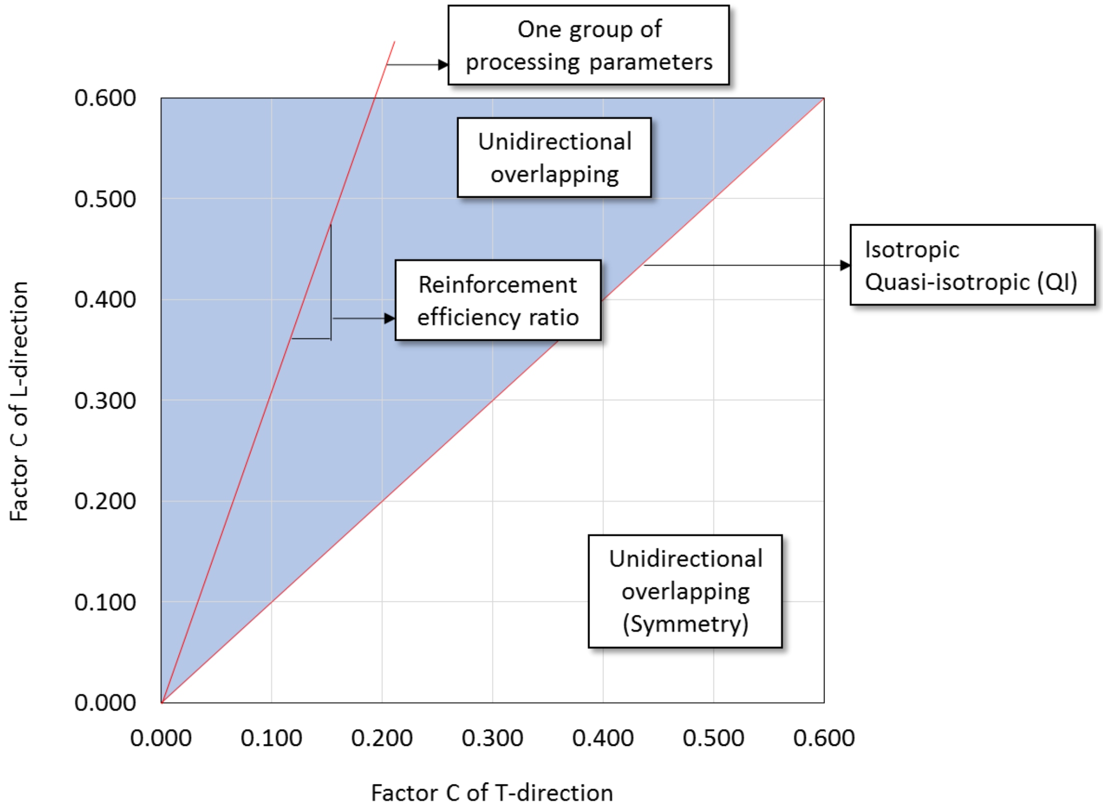


Figure 3-27 The composition of a development map

3.5.2. A brief discussion of how to use the map

There are three main categories of discontinuous CFRTP materials are discussed in this development map: quasi-isotropic materials, non-stretched CWT and stretched CWT. The Factor Cs for flexural properties are all listed in Table 3-4.

There are two types of materials in quasi-isotropic materials, one is CPT materials and the other is CTT materials. Both CPT and CTT materials are fabricated with water agent. The water is sued to distribute the fiber tapes and fibers of CPT and CTT materials. After careful stirring the mixture in water, the fiber tapes and the fibers will be uniformly distributed in-plane. Therefor we assumed that CTT and CPT materials are isotropic materials. As shown in Figures 3-28 and 3-29, the Factor Cs of CTT and CPT materials are treated as same on both directions.

CWT materials are fabricated by a carding process, which is a continuous fabricating process. The continuous movement will induce the fiber inclined along the moving direction, therefore the mechanical properties are different on L-direction from T-direction as shown in Table 3-3 and in Figures 3-28 and 3-29.

The critical process in CWT development, the stretching process will cause the fibers more inclined along the stretching direction, which is also the moving direction of carding process. In this study, the CWT materials were investigated with unidirectional stacking method. From Figure 3-28, the positions of non-stretched CWT materials are on the lings of similar slopes. Therefore, the fabricating parameters are closed to each other. After stretching process, the FOD of CWT materials will be improved. The lines of S-CWT30 and S-CWT40 materials are of similar slopes. However, the slope of S-CWT materials is much higher than that of CWT materials, which means that the difference of reinforcement efficiency of S-CWT materials is much larger than that of CWT materials. It is therefore confirmed that the stretching process can improve the reinforcement efficiency of CWT materials. Because the fiber components are same, the improvement is contributed by the increased FOD.

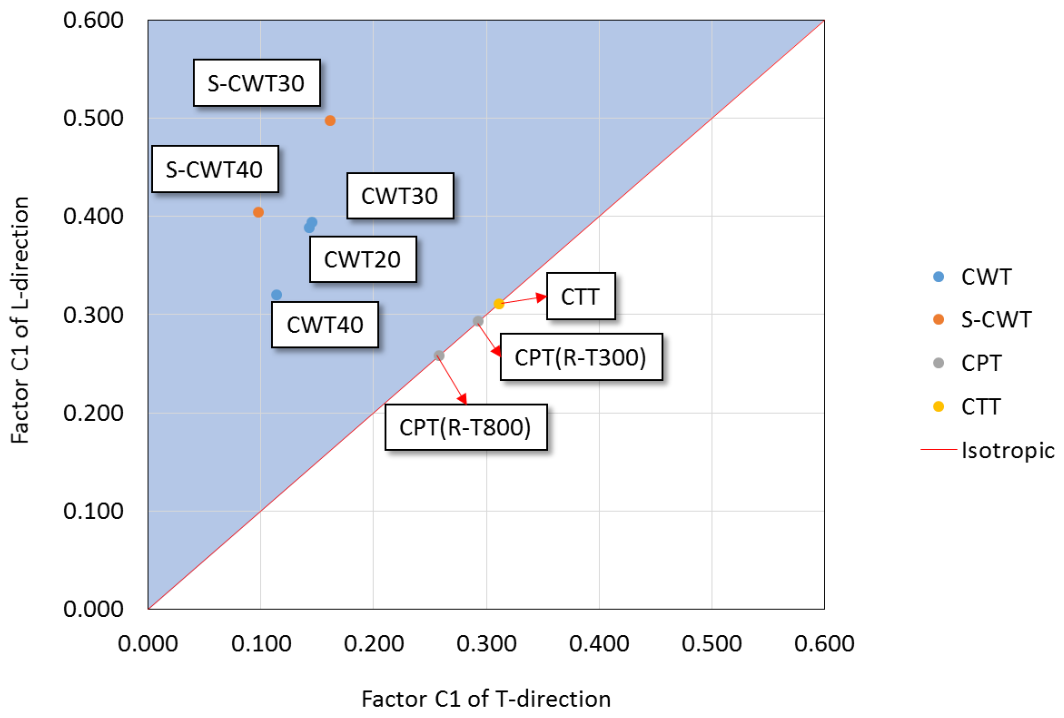


Figure 3-28 A development map of current discontinuous CFRP materials based on Factor C_1

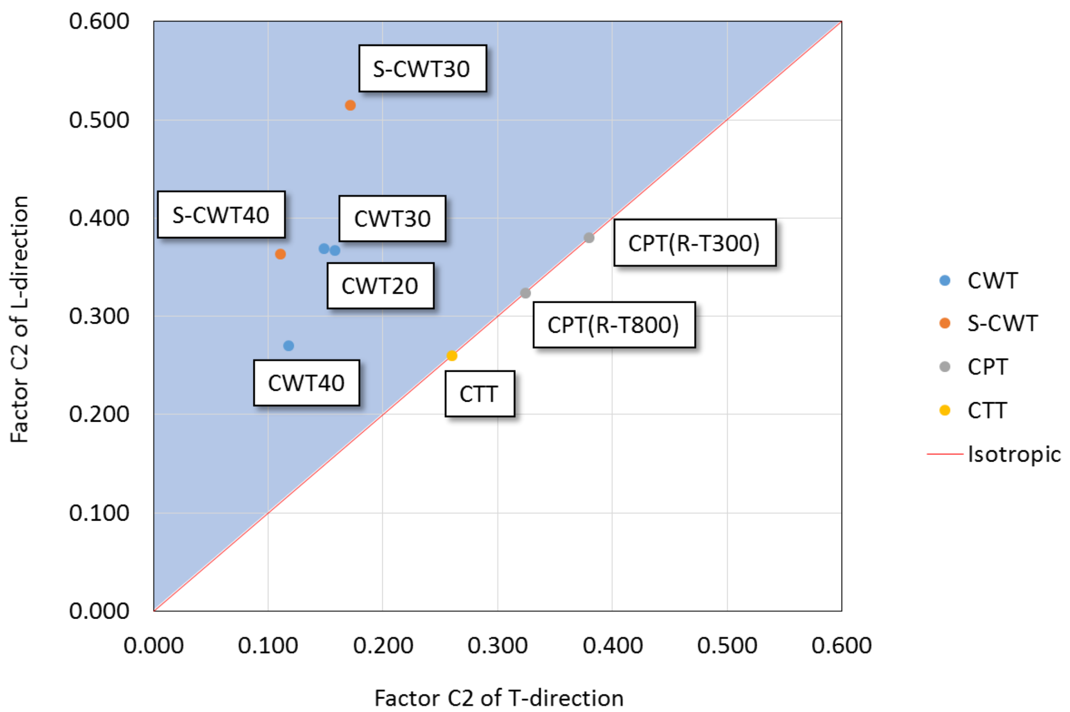


Figure 3-29 A development map of current discontinuous CFRTP materials based on Factor C_2

3.6. Summary

i. In order to further understand how to develop the applications of rCF, a modified rule of mixture was introduced to determine the reinforcement efficiency parameters, Factor Cs.

ii. Different from simple comparing the mechanical properties, Factor Cs are only contributed by FOD, FLD and internal defects, which is confirmed by the Factor Cs of mix-CPT and CPT(rCF/GF).

iii. A carding process is introduced to understand the effect of alignment process on the Factor Cs. The more aligned CF induce higher Factor Cs.

iv. Based on the Factor Cs of isotropic and anisotropic materials, a development map built on Factor Cs on L- and T- direction was introduced.

Chapter 4. A quantitative determination of alignment degree

4.1. A critical step to development re-manufacturing – alignment process

4.1.1. Review of current investigations of alignment processes

Current re-manufacturing can use rCF to make mat structure thermoplastics. However, the V_f of mat structure thermoplastics is no more than 40% because of the discontinuous FLD and misaligned FOD. If the rCF can be aligned along with a same direction, the aligned rCF can be used for extended applications, such as chopped carbon fiber tape reinforced thermoplastics, as shown in Table 1-4. If the alignment of rCF is improved, the V_f of chopped carbon fiber tape reinforced thermoplastics can be increased over than 50%, which will improve the potential of mechanical properties. Therefore, alignment process will be a critical step during development of rCF applications.

However, no promising alignment methods exist for rCF, which is randomly oriented because of the recycling processes used. After reviewing the current researches of alignment process, there are two prototypes of alignment processes as shown in Figure 4-1 and in Figure 4-2. However, both of them have limitation on FLD of rCF. The moment change of longer fibers seem difficult.

As shown in Figure 4-1, the fibers being suspended in water will hit the inclined plates. By the fiber orientation mechanism that the fibers will be aligned by the secondary plate. The aligned fibers will be continuously positioned on the mesh. After drying, aligned chopped fiber strand is therefore received [31].

A hydrodynamic alignment process developed by the University of Nottingham was shown in Figure 4-2. The fibers will be aligned by rotating drum with the contribution of vacuum power [29].

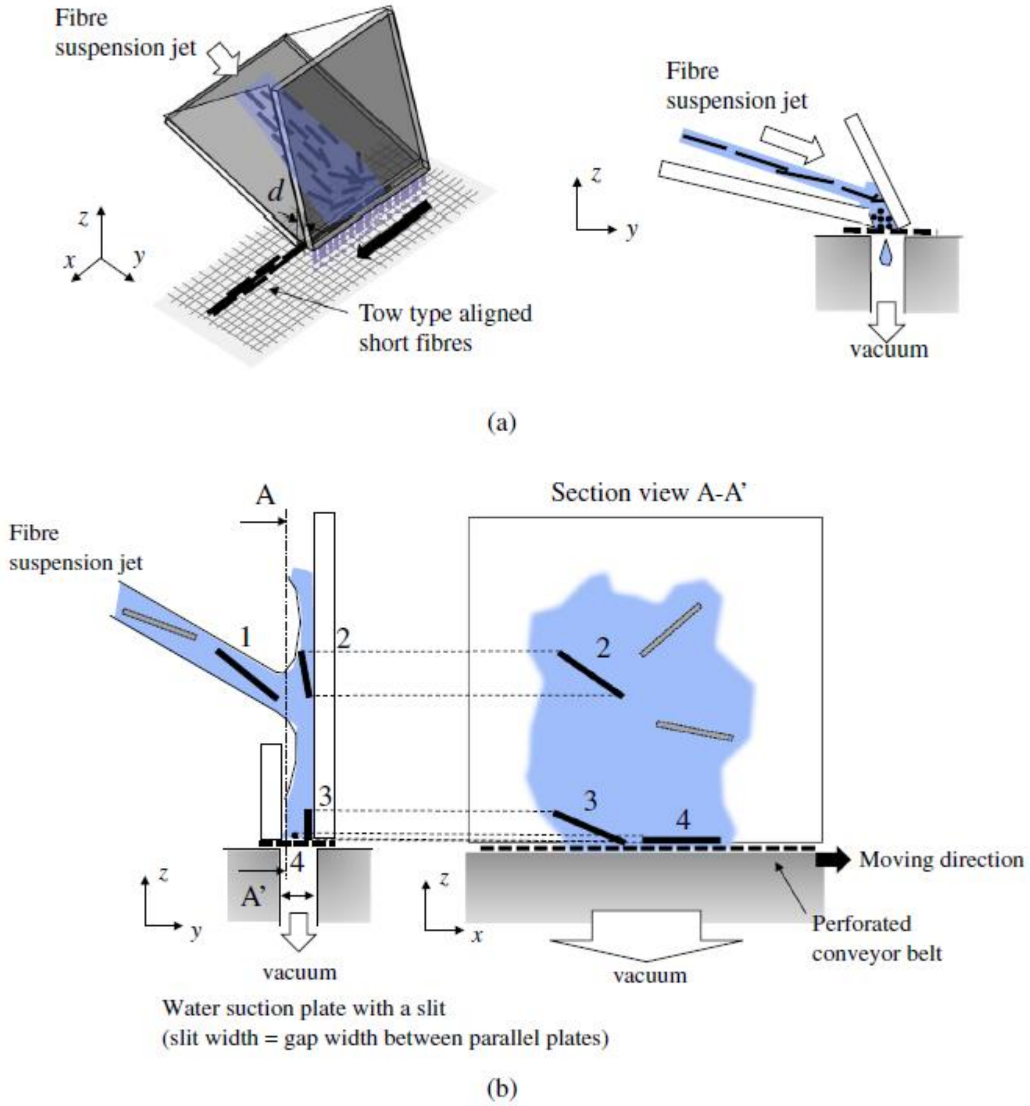


Figure 4-1 Schematic drawings of new discontinuous fiber alignment method: (a) initial concept and (b) simplification of the orientation mechanism [31].

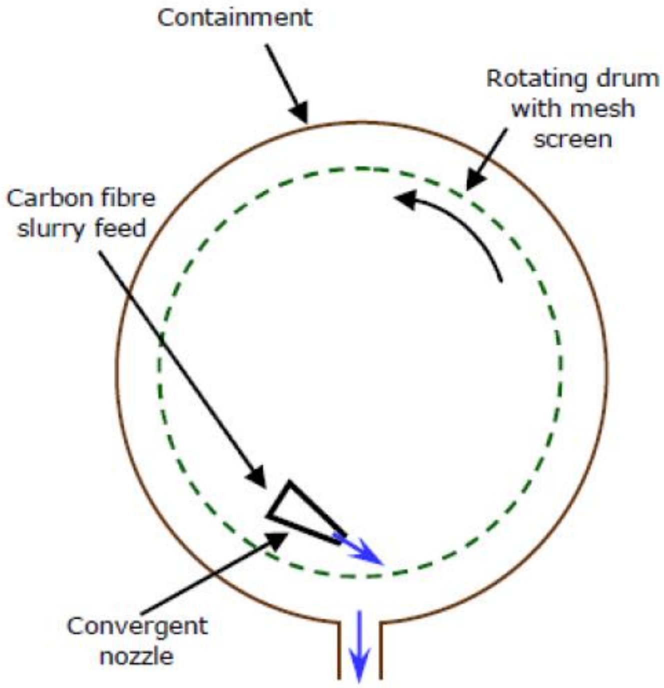


Figure 4-2 A schematic representation of the fiber alignment rig [29].

4.1.2. Difficulty to guide the development of alignment process

4.1.2.1. Negative factors in Factor Cs

The Factor C_1 and C_2 of mix-CPT(0.4/0.6) and CWT materials are shown in Figure 4-3. Factor C_1 is higher than C_2 for the CPT materials, on the contrary, the Factor C_1 is lower than C_2 for the CWT materials. Based on the characteristics of the papermaking process, the CF will be uniformly mixed with matrix resin fibers. Additionally, the CF and matrix resin fibers will be uniformly distributed. After compression molding, the web structure of CF will be enhanced. The enhanced CF web can bear more strain and then improve the flexural strength. The enhanced CF web structure, based on Figure 4-3, improved the reinforcement efficiency more in flexural strength than in flexural modulus.

Based on the characteristics of carding process, the CF will be fabricated with the fabrication of the matrix reins fibers, therefore, the areal density of CWT preforms is not as uniform as that of CPT preforms. The dense area in CWT preform will increase the difficulty of resin wetting.

During loading, this kind of area will induce stress concentration, which will make the failure start earlier. Therefore, the not uniform distribution of CF cannot maintain the reinforcement efficiency in flexural strength.

From Figure 4-3, the Factor C_1 and C_2 of CWT20 and CWT30 are almost as same as each other. In order to increase the V_f of CWT materials, the fabricating parameters will be adjusted to improve the fiber arrangement, which will theoretically increase the Factor C_1 and C_2. However, the Factor C_1 and C_2 are lower in CWT40. Even though the V_f of CWT is over than 40%, the void content is over than 5%, which is not acceptable for structural materials. The voids are caused by poor impregnation.

Even though Factor Cs can be used as guideline to develop the discontinuous CFRTP materials, they are still affected by internal defects such as voids. As discussed before, alignment process is critical step for further development of materials. Therefore, we need a more specific index to determine the improvement of fiber orientation distribution (FOD).

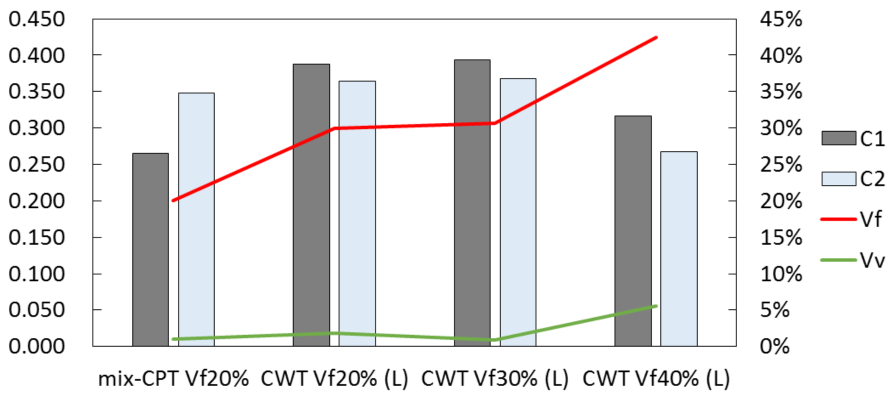


Figure 4-3 Factor Cs of different materials of different V_f and Vv

4.1.2.2. Current investigation approaches to determine fiber orientation distribution (FOD)

Conventionally, there are two categories of FOD investigations. The first one is direct analysis, in which the distributed fibers will be taken pictures. An image analysis will be chosen to process the pictures, after which the FOD will be measured, as shown in Figure 4-4. Usually, statistical approach is chosen to do a curve fitting. Based on the different concentration of the statistical curves, the different alignment quality will be qualitatively determined.

The second way to determine the alignment quality, mechanical experiments will be conducted to measure the specimens of same V_f but of different alignment quality, as shown in 4-1. Based on the discrepancy of the mechanical properties, the alignment quality of the correlative process will be therefore determined.

However, there is no direct quantitative value to describe the alignment quality of alignment process.

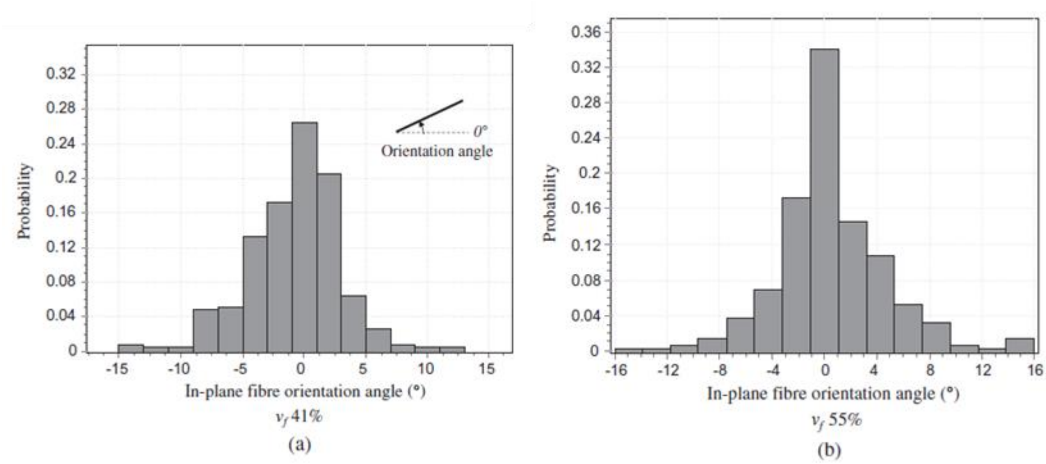


Figure 4-4 Probability density function of in-plane fiber orientations of composite specimens: (a) 41% of fiber volume fraction and (b) 55% fiber volume fraction [31].

Table 4-1 Average flexural properties of the composite laminate [29]

Specimen	Flexural strength, MPa	Flexural stiffness, GPa
Along to the alignment	1247.92 ± 68.48	81.84 ± 5.02
Perpendicular to the alignment	107.36 ± 2.07	7.23 ± 0.16

4.2. A statistical model for FOD determination

4.2.1. Introduction of a two-parameter exponential equation

In this study, FOD will be determined with an equation proposed by Xia et al. [32] as shown in Eqn. 4.1. A good FOD function should have the property that it has the shape parameters describing a change from a unidirectional distribution to a random distribution.

$$g(\theta) = \frac{\{\sin\theta\}^{2p-1}\{\cos\theta\}^{2q-1}}{\int_{\theta_{min}}^{\theta_{max}}\{\sin\theta\}^{2p-1}\{\cos\theta\}^{2q-1}\,d\theta} \tag{4.1}$$

Where, p and q are the shape parameters which can be used to determine the shape of the distribution curve, as shown in Figure 4-5.

The mean fiber orientation, θ_{mean}, can be derived from Eqn. 4.2 as follows:

$$\theta_{mean} = \int_{\theta_{\min}}^{\theta_{\max}} \theta g(\theta) d\theta \tag{4.2}$$

For example:

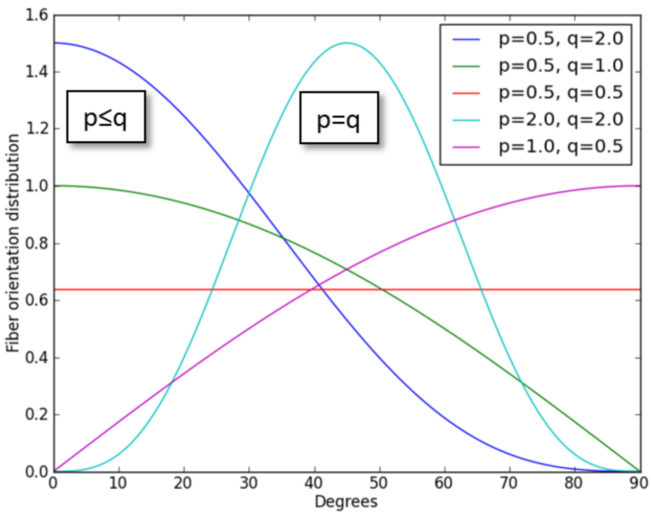


Figure 4-5 An example of the two-parameter exponential equation of different shape parameters

4.2.2. Determination of alignment degree

Based on the Eqn. 4.1, the fiber orientation coefficient, f_θ, is therefore defined as Eqn. 4.3.

$$f_\theta = 2\int_{\theta\min}^{\theta\max} g(\theta)\cos^2(\theta)d\theta - 1 \qquad (4.3)$$

When f_θ=-1, all fibers lie perpendicular to the loading direction; f_θ=0 corresponds to a random distribution in the angle θ; f_θ=1 implies all fibers are aligned parallel to the loading direction. Therefore, these characteristics make the fiber orientation coefficient suitable to be used as alignment degree, which will be discussed in detail in later sections. The explanation of resultant graph of alignment degree is shown in Figure 4-6.

Table 4-2 The characteristics of Eqn. (4.2)

f_θ	Description
-1	All fibers ⊥ The loading direction
0	A random distribution in the range θ
1	All fibers // The loading direction

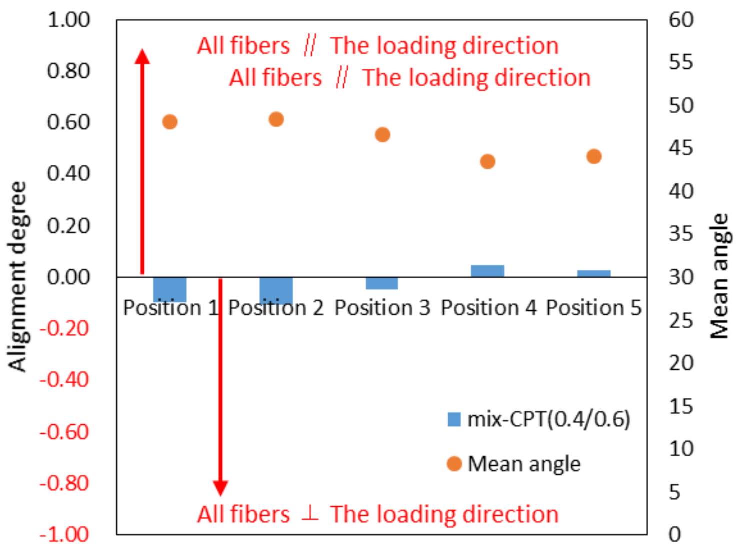


Figure 4-6 Explanation of the graph of alignment degree

Table 4-3 Examples of alignment degrees of different shape parameters

p	*q*	Mean degree	Alignment degree
0.5	2.0	23.2	0.600
0.5	1.0	32.7	0.333
0.5	0.5	45.0	0.001
2.0	2.0	45.0	5.905
1.0	0.5	57.3	-0.333

4.3. Applying the statistical model on CPT and CWT

4.3.1. Basic information of materials

In this chapter, paper making process and carding process were used as shown in Table 4.4. Mix-CPT(0.4/0.6) is especially used to check this approach to describe the FOD and determine the alignment degree based on averaged fiber diameter. CWT materials of different V_f are used in order to illustrate the FOD more clearly. The basic material information in details are listed in Table 4-4.

In this research, laser-microscope was used to determine the FOD of each material type, which will be introduced in details in Section 4.3.1. Figure 4-7 shows the pictures of cross section of each material type.

Table 4-4 The materials used for this approach

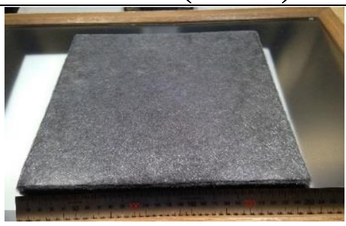
Material	Mix-CPT(0.4/0.6)	CWT
Actual images		
Fabricating process	Paper-making process	Carding process
Suspension agent	Water	None
Areal density	Uniform	Varies in positions
Volume fraction	20%	20%, 30%, 40%
FOD	Uniform	Aligned
D_{ave} (μm)	6.2	7

Table 4-5 The basic information of materials and the parameters p and q for Eqn. 4.1.

Materials	CPT	CWT		
Fiber type	R-T300&R-T800	T700		
Matrix resin	PA6 (fibers)	PA66 (fibers)		
d_{ave} (μm)	6.2	7		
V_f	20.0% (0.4/0.6)	29.9%	30.7%	42.4%
V_v	1.0%	1.9%	0.9%	5.6%
Parameter p	1.857	1.089	1.127	0.976
Parameter q	1.736	1.810	1.944	1.900

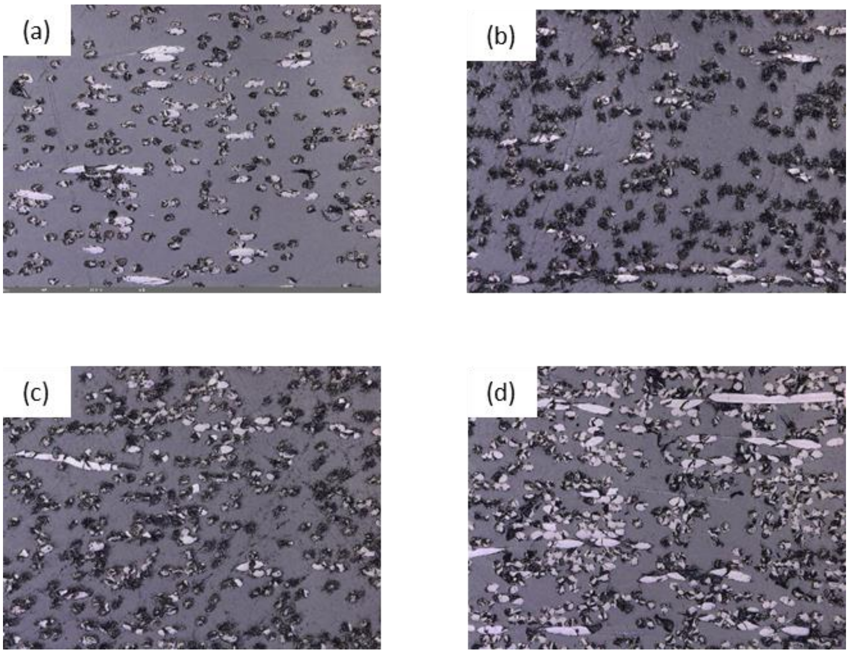


Figure 4-7 The pictures taken from laser microscope: (a) mix-CPT(0.4/0.6); (b) CWT20(L); (c) CWT30(L); (d) CWT40(L)

4.3.1. Measuring FOD by laser-microscope

In this study, a simple observation approach was conducted to measure the fiber orientations, provided by Lee et al, as shown in Figure 4-7. Even though the FOD should be determined in three-dimensional system of coordinate, the out-of-plane FOD can be ignored in this paper because the fiber length is much larger than one single ply. The cross-section of the thickness direction is polished for clear picture. Fiber orientation is defined as the angle between the fiber axis and the normal direction of the cross-section and it is calculated by the Eqn. 4.4 [33].

$$\theta = \arccos\left(\frac{d}{l}\right) \tag{4.4}$$

Where, θ is the inclination angle of fibers, d is the diameter of rCF and l is the in-plane projection length of rCF. Fiber spots on one specimen will be measured and almost two hundred to three hundred data points will be counted. Then the data will be further used for curve fitting with the Eqn. 4.1.

In this research, fiber length is much larger than ply thickness, only in-plane FOD is measured. l is projection length of each fiber cross section on the axis perpendicular thickness direction. The measuring approach is shown in Figure 4-8. The fiber orientation angle is calculated by Eqn. 4.3. 5 random positions on one specimen are observed. The measured FOD will be curve fitted with Eqn. 4.1. Shape parameters, p and q, are obtained from curve-fitting, as shown in Figure 4-9. The shape parameters of these 5 position will be averaged in order to determine those of the specific material.

Curve-fitting will be conducted in Python 2.7. The details will be introduced in Appendix I.

Table 4-6 An example of the determination of shape parameters for one specimen

Mix-CPT(0.4/0.6)	*p*	*q*
Position 1	1.656	1.368
Position 2	1.971	1.595
Position 3	2.200	1.991
Position 4	1.603	1.765
Position 5	1.856	1.959
Average	**1.857**	**1.736**

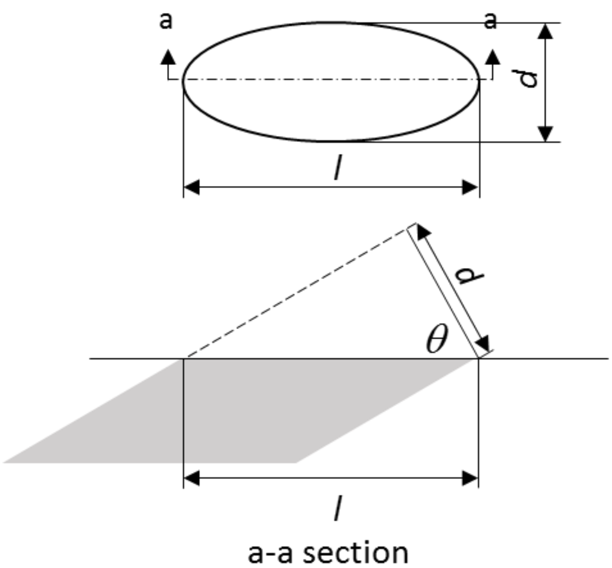


Figure 4-8 A schematic image for FOD determination [33].

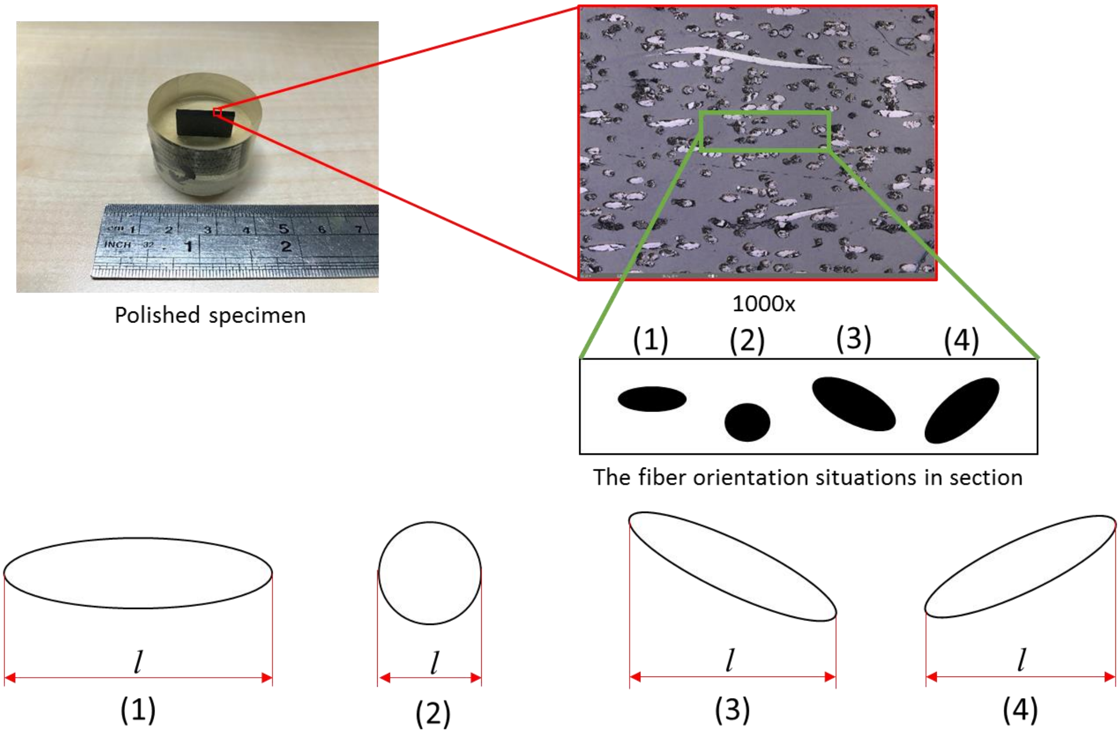


Figure 4-9 The measuring method to determine the FOD.

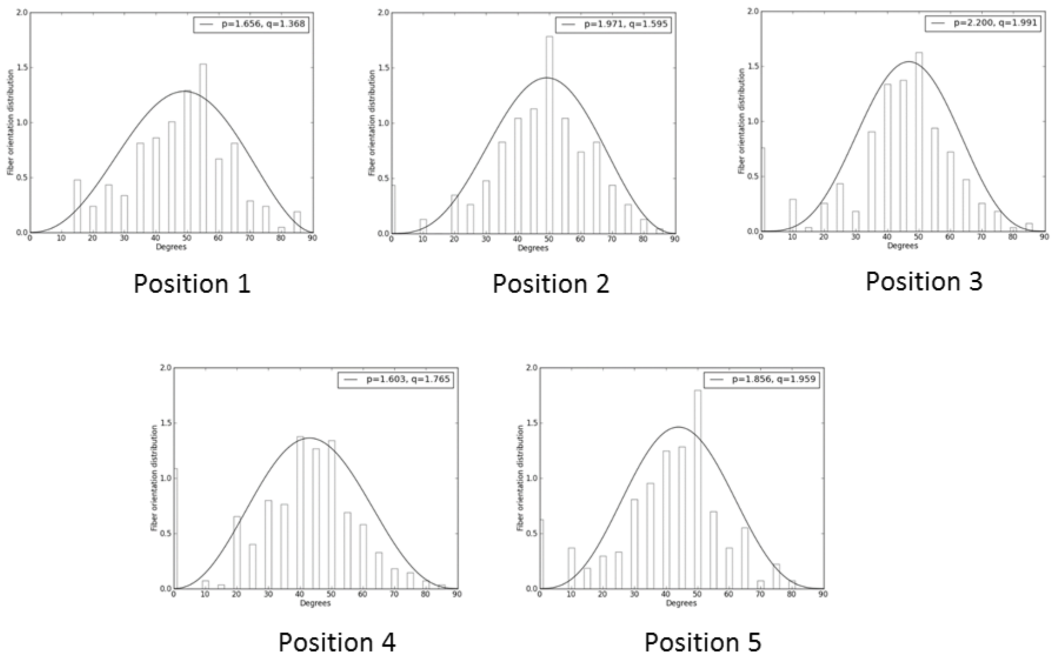


Figure 4-10 Curve fitting for 5 random positions on one cross-section

4.3.2. Alignment degree of CPT and CWT

4.3.2.2. Results and discussion

As discussed in Section 4.1, Factor C cannot be directly used as alignment degree. Therefore, in this paper, the fiber orientation coefficient in Eqn. 4.3 is used as the definition of alignment degree. This equation can identify the change of FOD from unidirectional distribution to random distribution. When the results is -1 or +1, it means the fibers are all aligned along the direction normal or parallel to loading direction. When the result is 0, the fibers are randomly orientated. These characters of this equation makes it a rational definition of the alignment degree. Once the alignment degree has been illustrated, the industries can use it as an instructive parameter to improve their processing parameters without conducting actual mechanical experiments, which are time and labor consumption.

Even though a simple observation approach was used in this paper, the results clearly showed the difference of FOD in different materials and can clearly illustrate the value of the alignment degree.

As shown in Figure 4-11, the peak of FOD for CWT materials slightly moved leftward compared with mix-CPT, which is considered of uniformly random fiber orientations. The important parameters determining the FOD and alignment degree are shown in Table 4.5. Based on Eqns 4.2 and 4.3, the alignment degrees and mean degrees of mix-CPT and CWT materials are shown in Figure 4-12. The alignment degree of mix-CPT is around 0.265, which is closed to 0.0. Based on the definition of alignment degree in this chapter, this number can be considered to confirm the randomly orientated fiber architecture of mix-CPT, which is in accordance with characteristics of the prototype papermaking process. This can also be confirmed by the mean degree of mix-CPT is around 45° and that of CWT is around 35°. Compared within the CWT materials, the alignment degree increases with V_f. This trend illustrates that if the alignment degree increases, the potential V_f of CWT materials can also be increased. Based on the rule of mixture, increased V_f will potentially contribute to the mechanical properties. However, in this study, the void content is still high in CWT with 42.4% of V_f even though the alignment degree is apparently increased. Therefore, higher $V_{f,}$ especially over than 40%, it is necessary to increase the alignment degree of a much higher level.

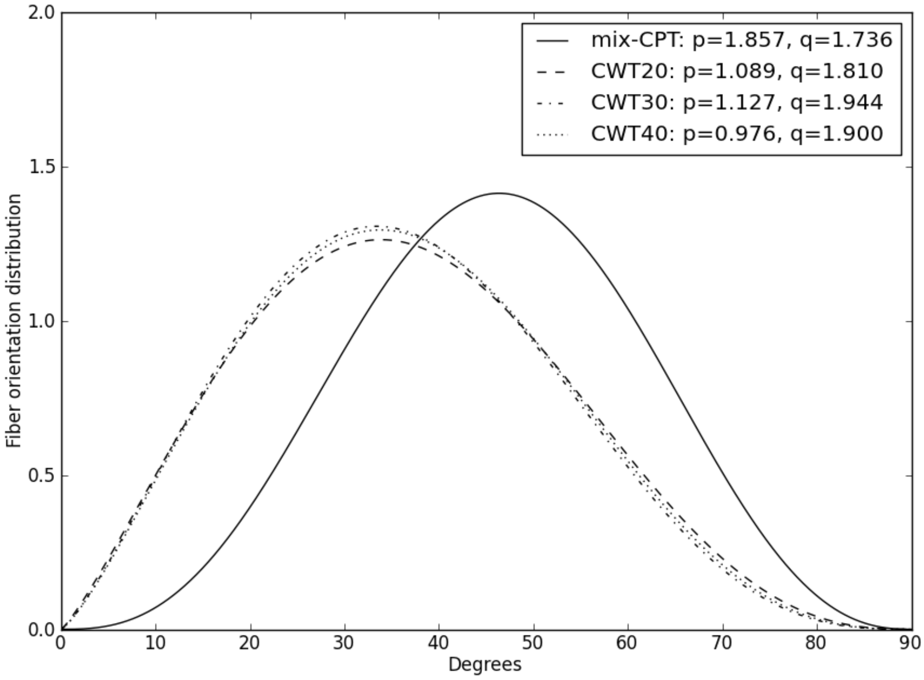


Figure 4-11 Fiber orientation distribution of mix-CPT and CWT materials

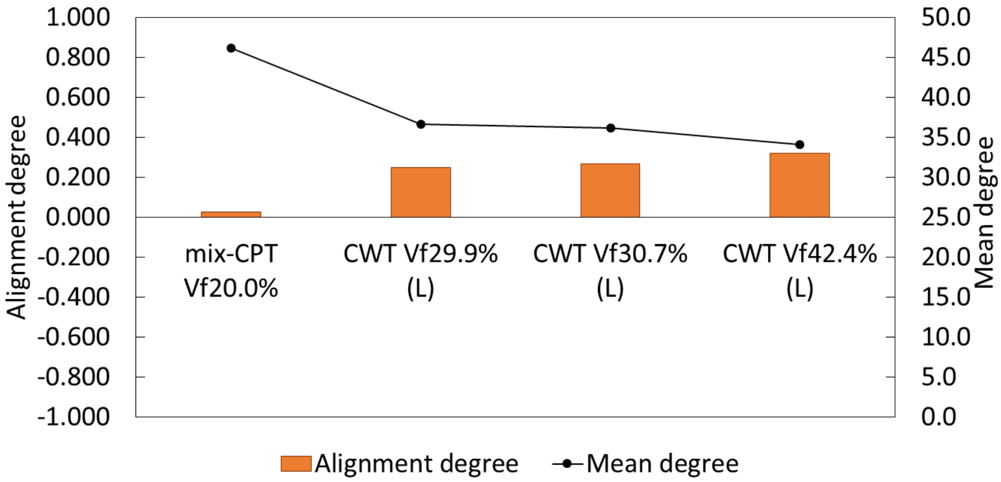


Figure 4-12 The alignment degree of different materials

4.4. A further discussion of alignment degree

4.4.1. The relation between alignment degree and flexural modulus

Figures 4-13 and 4-14 show the relations between the alignment degree and the mechanical properties. Even though the potential factors influencing the mechanical properties have been discussed, such kind of schematic map can be drawn for different rCFRTP systems. In CWT material system, if alignment degree is increased by 0.01, the flexural modulus and strength will be increased by 0.5 GPa and 16.4 MPa respectively. Furthermore, the V_f is the most concern of the applications of rCF. Based on this paper, if the alignment degree can be effectively increased by 0.01, the potential V_f can probably be increased by 2%, as shown in Figure 4-15.

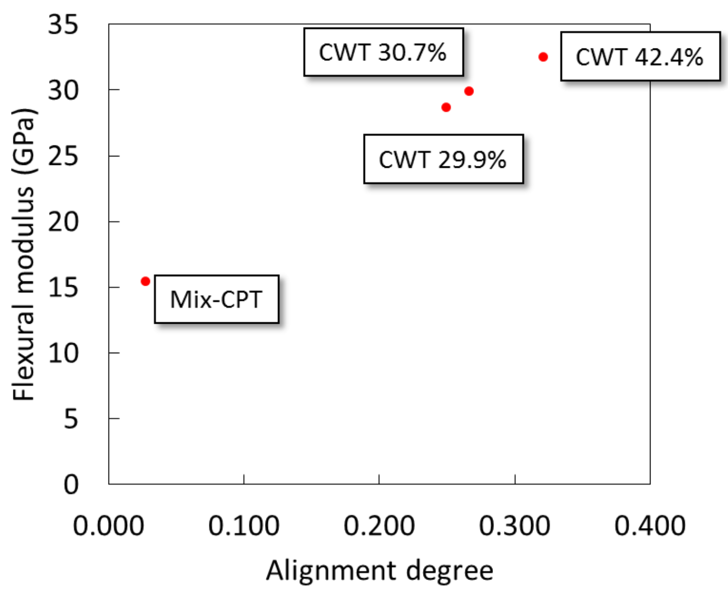


Figure 4-13 The relation between alignment degree and flexural modulus

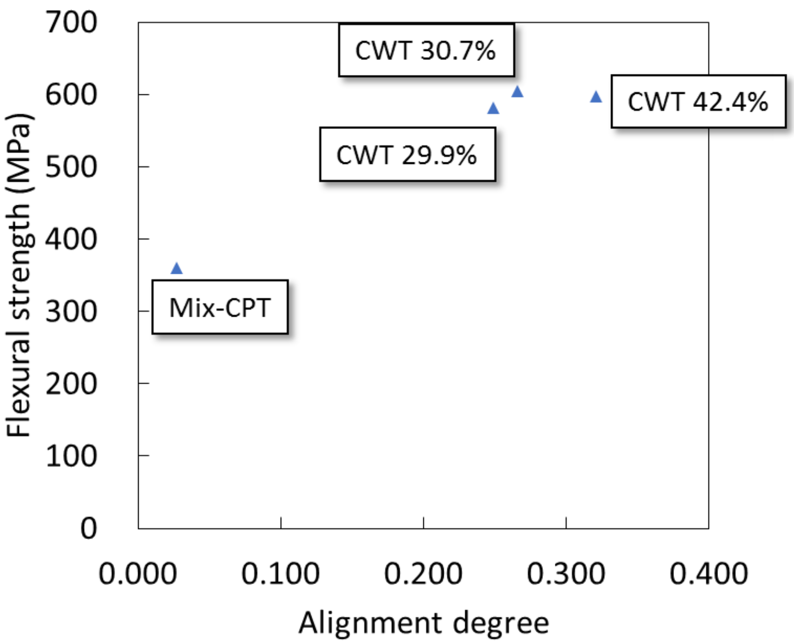


Figure 4-14 The relation between alignment degree and flexural strength

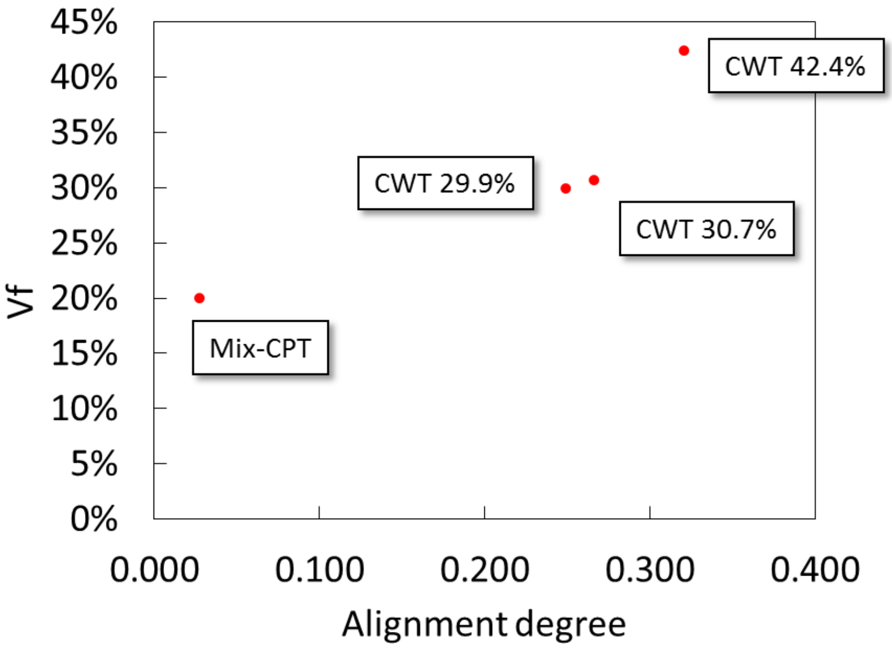


Figure 4-15 The relation between alignment degree and V_f

4.4.2. The relation between alignment degree and Factor Cs

After discussing the relations between alignment degree and material properties, it is found that the flexural modulus and V_f are enhanced with the increase of alignment degree. Furthermore, the improvement can also happen in flexural strength during the void content of materials is no more than 2%. If the void content is higher than 2%, the flexural strength will decrease even though the alignment degree is increased, as shown in Figure 4-14.

As discussed in Chapter 3, the mechanical properties of materials will be affected by not only the component properties but also the V_f of the components. Therefore, Factor Cs were introduced to discuss the reinforcement efficiency by removing the interference caused by material properties and content of each component. In this section, the relation between Factor Cs and alignment degree will be built and therefore discussed.

There are two types of Factor Cs, Factor C_1 is for flexural modulus and Factor C_2 is for flexural strength. Depending on the continuity of manufacturing process, the Factor Cs on L-direction (moving direction) and on T-direction are different. The difference is considered to be caused by the fiber alignment. By simply logic reasoning, the ratio between Factor C, as shown in Eqn. 4.5, on L-direction and that on T-direction is capable of illustrating the alignment quality caused by alignment process.

$$\frac{Factor\ \mathrm{C\ of\ L{-}direction}}{Factor\ \mathrm{C\ of\ T{-}direction}} \tag{4.5}$$

Figure 4-16 shows the relations between the alignment degree and the Factor Cs on L-direction. Even though the Factor Cs increase when the alignment degree is increased, the Factor Cs of CWT40 significantly decreased compared with CWT30, which is mainly induced by the void content.

Figure 4-17 shows relations between the alignment degree and the reinforcement efficiency ratio. It is confirmed that the reinforcement efficiency ratio is capable of illustrating the improvement of fiber alignment after stretching process. However, the alignment degree between different materials of similar fabricating process cannot be identified. As shown in Figure 4-17, the reinforcement efficiency ratios are almost similar with each among CWT materials.

Therefore, alignment degree is necessary to identify the quality of alignment process or fabricating process because reinforcement efficiency, Factor Cs, are not clear enough to distinguish the situation of FOD among different materials.

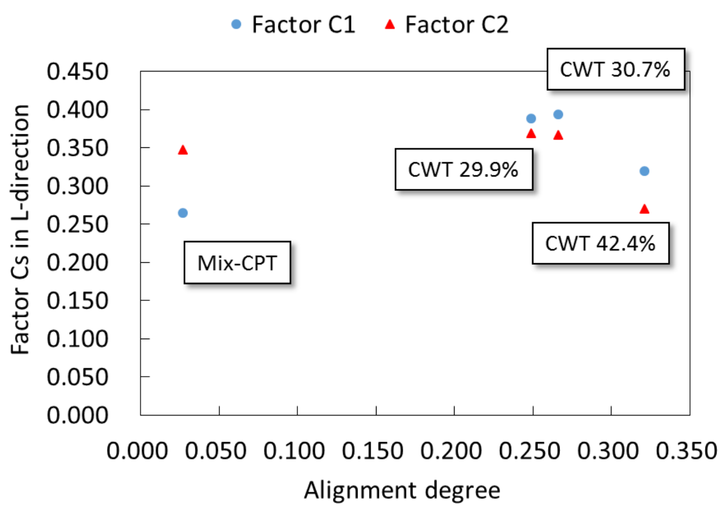


Figure 4-16 Relation between alignment degree and Factor Cs

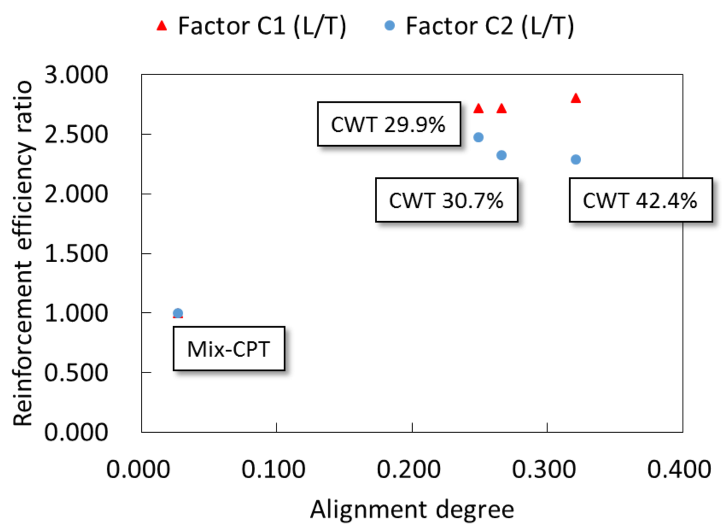


Figure 4-17 Relation between alignment degree and reinforcement efficiency ratio

Table 4-7 Factor Cs and reinforcement efficiency ratio of mix-CPT and CWT

Material	Alignment degree	Factor C_1			Factor C_2		
		T-direction	L-direction	Factor C_1 (L/T)	T-direction	L-direction	Factor C_2 (L/T)
mix-CPT(0.4/0.6) V_f 20%	0.027	0.265	0.265	1.000	0.348	0.348	1.000
CWT V_f 29.9%(L)	0.249	0.143	0.389	2.720	0.149	0.369	2.477
CWT V_f 30.7%(L)	0.266	0.145	0.394	2.717	0.158	0.367	2.323
CWT V_f 42.4%(L)	0.321	0.114	0.320	2.807	0.118	0.270	2.288

4.5. Summary

i. A two-parameter exponential equation is introduced to fit the FOD of discontinuous CFRTP materials.

ii. The derivative equation for fiber orientation coefficient fits the characteristics of alignment degree. Therefore the definition of alignment degree is proposed.

iii. The alignment degrees of mix-CPT and non-stretched CWT were measured. It is confirmed that the alignment degree is suitable to identify the different FOD of different materials.

iv. The connections between material properties (mechanical properties and V_f) and alignment degrees were discussed.

Chapter 5. Summary

5.1. Papermaking process to investigate re-manufacturing problems

Because current published recycling processes cannot reclaim recycled carbon fibers (rCF) of the fiber length distribution (FLD) and of the fiber orientation distribution (FOD) as same as fresh carbon fibers (CF). Therefore, how to re-manufacturing randomly oriented and discontinuous rCF is a problem. In this thesis, a paper making process was introduced to fabricate the rCF with thermoplastic resin fibers. Thermoplastics have attracted increasing attention because they can improve the molding cycle and can be easily reprocessed by heating. The resultant carbon fiber reinforced thermoplastics (CFRTP) are termed as carbon fiber paper reinforced thermoplastics, short as CPT.

However, there is a concern to reuse rCF that is the mixed types of reinforcement fibers with rCF after recycling process. Depending on the specific design considerations, the different carbon fiber reinforced plastics (CFRP) materials are overlapped and another kind of reinforcement fibers are added in order to gain synthetic mechanical properties. However, there is no practical method to sort and to separate different reinforcement fibers.

Before discussing the effect of mixed different fiber types, the proper compression molding pressures and the basic material properties of CPT materials were discussed. After comparing the flexural properties under 5 levels of compression molding pressure, 1 MPa, 3 MPa, 5 MPa, 8 MPa and 10 MPa, were investigated. During 3 MPa and 8 MPa, the flexural properties of CPT reinforced by R-T300 (recycled T300 fibers) and CPT reinforced by R-T800 (recycled T800 fibers) are good. After further discussion of the results of Izod tests, the impact energy absorption is highest under 5 MPa and 8 MPa. Therefore, it is recommended that the molding pressure should be set from 5 MPa to 8 MPa.

Two kinds of situations of mixed different types of reinforcement fibers were investigated based on the papermaking process. The first situation is the effect of mixed different types of rCF on the mechanical properties of rCFRTP materials, which was termed as mix-CPT in this thesis.

The second situation is the effect of another kind of reinforcement fibers, glass fibers (GF) in this thesis, on the mechanical properties of rCFRTP materials, which was termed as CPT(rCF/GF) in this thesis.

R-T300 and R-T800 fibers were mixed by papermaking process to make mix-CPT materials. Depending on the volume fraction (V_f) ratio of mixed rCF, there are 6 types of mix-CPT materials. From the results of three point bending tests, the flexural properties of mix-CPT materials will be varied with the change of V_f ratios, which is more significant for flexural strength. In the situation of CPT(rCF/GF) materials, the ductility of GF still contributes to the flexural properties. Even though the modulus of GF is much smaller than CF, 1% of rCF was replaced by GF and the flexural modulus was slightly improved. The flexural strength was affected by replacing the rCF by GF. But more GF ensured the flexural strength. Therefore, it is not a problem to reuse rCF even though the mixed types of reinforcement fibers cannot be separated.

5.2. Two indexes to guide the development of re-manufacturing process

It is the center problem in this thesis that is how to re-manufacture rCF. In order to contribute to extending the applications of rCF, two indexes were introduced and discussed in this thesis. The first one is reinforcement efficiency factors, Factor Cs, which are derived from the modified rule of mixtures (MRoM). Based on the experiment results of three point bending tests and component material properties, the Factor C_1 of flexural modulus and C_2 of flexural strength were calculated. In order to discuss the value of Factor Cs, carbon fiber card web reinforced thermoplastics (CWT) made by a carding process were used to investigate the flexural properties. Based on the continuous movement of carding process, the molded CWT plates were different in mechanical properties along the L-direction (moving direction) and along T-direction. Based on the calculations, Factor Cs are clearer to illustrate the internal fiber architectures due to different manufacturing process by removing the interference of component material properties and that of V_f of the components. In order to further extend the value of Factor Cs, a development map was built based on Factor Cs of different materials with considering the isotropic and anisotropic properties. The map is able to help the manufacturers to understand where their products locate among the similar materials in market. Additionally, this map can help to adjust the alignment process, which is a critical process in manufacturing rCF, in a direct way.

The second index is alignment degree. Even though the Factor Cs can contribute to developing the manufacturing process and the relative rCFRTP materials, they are negatively affected by the internal defects, such as void content. Therefore, an index is necessary to identify the quality of alignment process in re-manufacturing rCF. In thesis, a direct simple quantitative value was introduced based a two-parameter exponential equation. The characteristics of this value made it practical to be the alignment degree. Different from conventional qualitative approach, the alignment degree can be used to connect the FOD of rCFRTP materials with the alignment quality, mechanical properties and V_f in an analytical way. A brief discussion was conducted to compare the Factor Cs and alignment degree. Factor Cs are more practical to guide the development of rCFRTP materials and help to describe the possible mechanical properties based on relative manufacturing process. Alignment degree is more practical to determine the quality of alignment process. One single value made it possible and analytical to compare the FOD of different materials by different alignment processes.

5.3. Achievements

This thesis introduced a papermaking process to re-manufacture rCF. The CPT materials showed more promising mechanical properties and more cost-benefit than other published rCFRTP materials.

Two index, Factor Cs and alignment degree, were proposed to help the manufacturers to develop their manufacturing process and to improve the possible alignment process in a clear way. A development map built on Factor Cs is able to understand where a specific rCFRTP material locate among the similar materials. This map can also illustrate the development direction for alignment process. The other index, alignment degree, is much more specific index to quantitatively determine the FOD with a single value. The single value can be used to connect the possible material properties to help the manufacturers understand how to improve their alignment processes.

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Appendix I: Curve fitting in Python

Code in Python 2.7
Edited in Jupyter Notebook
Packages: numpy, matplotlib, scipy.optimize

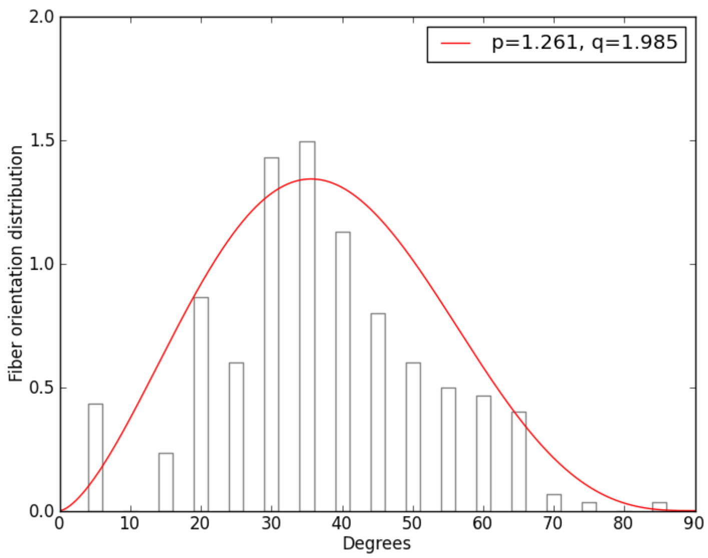
Input:

```
"""
Laser microscope curve fitting data curve fitting
CWT L30

Position 2
"""

import numpy as np
from matplotlib import pyplot as plt
from scipy.optimize import curve_fit

def FOD(x, p, q):
    basic = (np.sin(x))**(2.*p-1. * (np.cos(x))**(2.*q-1.)
    result = basic / np.trapz(basic, x)
    return result

def deg2rad(degrees):
    result = np.pi * degrees / 180.
    return result

def rad2deg(radians):
    result = 180. * radians / np.pi
    return result

a = deg2rad(0.)
b = deg2rad(95.)


x = np.arange(a, b, deg2rad(5.))

z = np.linspace(deg2rad(0.), deg2rad(90.), 1000)
zz = np.linspace(0., 90., 1000)

ydata =
[0.,0.432,0.,0.233,0.864,0.598,1.429,1.495,1.13,0.797,0.598,0.498,0.465,0.399,0.066,0.033,0.
,0.033,0.]
```

```
popt, pcov = curve_fit(FOD, x, ydata)

p = popt[0]
q = popt[1]

y = FOD(z, p, q)

print p, q

plt.bar(rad2deg(x)-1, ydata, width=2., color="white", edgecolor='grey')
plt.plot(zz, y, color="red", label='p=%.3f, q=%.3f' %(p, q))

plt.legend()
plt.xlabel('Degrees')
plt.ylabel('Fiber orientation distribution')
plt.xlim(0., 90.)
plt.ylim(0., 2.)
plt.show()
```

Output:

```
1.26110275265 1.98473084394
```



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