

Doctoral Dissertation (Shinshu University)

**Development of the low-cost and high-value
recycling method of fiber reinforced plastic**

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CHAPTER ONE

Introduction

Chapter1 Introduction

1.1 Fiber reinforced plastic and recycling

A composite is a structural material that consists of two or more combined constituents that are combined at a macroscopic level and are not soluble in each other. One constituent is called the reinforcing phase and the one in which it is embedded is called the matrix. The reinforcing phase material may be in the form of fibers, particles, or flakes. The matrix phase materials are generally continuous. Examples of composite systems include concrete reinforced with steel and epoxy reinforced with graphite fibers, etc. In this study, reinforcing phase is fiber and matrix phase is resin. It is called fiber reinforced plastic (FRP) (also fiber reinforced polymer).

FRP composites are engineered structures that commonly comprise a soft matrix, typically a plastic, encapsulating stiffer, load-bearing filler in the form of fibers or particles. For high-strength composites, the fibers should be stiff and have a high aspect ratio (length-to-width ratio). This allows a good transfer of load from the matrix to the filler when the composite is put under mechanical stress.

As the characteristic referenced above, FRP composite materials have been widely used in various industry fields, such as aerospace industry, automotive industry, marine industry and wind energy industry, due to their interesting combination of properties, strength, durability, high strength-to-weight ratios, heat resistance and corrosion resistance. Today, it is hard to find an industry in which FRP composite materials are not used. The global glass fiber reinforced plastic (GRFP) composites market will total US\$29.4 billion in 2013[1]. Global volume demand for carbon fiber reinforced plastic (CFRP), estimated at around 67 thousand tons in 2012, is expected to maintain a

2012-2020 compound annual growth rate (CAGR) of 15.3% to reach 210 thousand tons by 2020. In terms of value, demand for CFRP, estimated at US\$10.25 billion in 2012 is expected to record a CAGR of 11.9% over 2012-2020 in reaching US\$25.2 billion by 2020. In tandem with the CFRP market, global demand for carbon fibers in terms of volume, estimated at 45 thousand tons in 2012 and forecast to be 51.7 thousand tons in 2013, is further projected to reach 141 thousand tons by 2020, registering a 2012-2020 CAGR of 15.4%. In terms of value, consumption of carbon fibers globally is estimated to stand at US\$2.03 billion in 2012 and projected to reach around US\$5 billion by 2020[2].

Despite all advantages associated with FRP, the increasing use generates also an increasing amount of FRP waste. Common sources of waste include out-of-date pre-pregs, manufacturing cut-offs, testing materials, production tools and end-of-life components. Recycling FRP is inherently difficult because of (i) their complex composition (fibers, plastic and fillers), (ii) the crosslinked nature of thermoset plastic (which cannot be remolded), and (iii) the combination with other materials (metal fixings, honeycombs, foam, etc.).

As a result, for many years FRP materials have been incinerated or used for landfill without any recycling efforts[3-4]. However, these are unsatisfactory solutions for several reasons[5]: (1)Environmental impact: the increasing amount of FRP produced raises concerns on waste disposal and consumption of non-renewable resources. (2)Legislation: recently established environmental laws in most developed countries make it illegal to use FRP for landfill. (3)Production cost: Fiber is very expensive, especially carbon fiber, both in terms of energy consumed during manufacturing and material price[6]. (4)Management of resources: demand of virgin fiber, especially

carbon fiber, usually surpasses supply-capacity[7], so recycled fiber could be re-introduced in the market for non-critical applications. (5)Economic opportunity: disposing of FRP by landfilling can cost approximately 52.5 Yen/kg in Japan (data from Faculty of Textile Science and Technology of Shinshu University); recycling would convert an expensive waste disposal into a profitable reusable material. Thus, environmentally friendly recycling methods must be established.

1.2 Recycling technologies of fiber reinforced plastic

A number of recycling technologies have been proposed and developed for thermoset composite materials and these are listed as follows. There are fundamentally three categories of process: those that involve mechanical comminution techniques to reduce the size of the scrap to produce recyclates; those that use thermal processes to break the scrap down into materials and energy; and those that are based on a reactive medium to decompose polymeric resin into relatively large oligomers while the fibers are subsequently collected.

1.2.1 Mechanical recycling

Mechanical recycling techniques have been investigated for both glass fiber and carbon fiber reinforced composites, but the most extensive research has been done on glass fiber. The technique involves breaking-down the composite by shredding, crushing, milling, or other similar mechanical process. It is usually to initially size reduce the scrap composite components in some primary crushing process. This would typically involve the use of a slow speed cutting or crushing mill to reduce the material to pieces in the order of 50-100 mm in size. This facilitates the removal of metal inserts and, if

done in an initial stage where the waste arises, the volume reduction assists transport. The main size reduction stage would then be in a hammer mill or other high speed mill where the material is ground into a finer product ranging from typically 10 mm in size down to particles less than 50 mm in size. Then a classifying operation, typically comprising cyclones and sieves, would be employed to grade the resulting recycle into fractions of different size. The resulting scrap pieces can then be segregated by sieving into powdered products (rich in resin) and fibrous products (rich in fibers) [8-13].

In Japan, FRP recycled as the raw materials and mineral fuel of cement. Waste FRPs were cut into 20 mm or less, and then they were supplied to the calcination preheating process of cement manufacture. Resin content, reused as fuel, can recycle energy. Fiber and filler, reused as materials of cement, can recycle materials. The feature of this method is it is not necessary to separate FRP into resin and fiber. It is not a perfect method, because it cannot be carried out without support of government. Processing cost, about 35yen/kg, is very expensive. It is higher than value of cement raw materials and mineral fuel, which is about 15 yen/kg.

1.2.2 Thermal processes

Pyrolysis and fluidized beds are the two methods that have been used to recycle FRP. Each technique removes the resin by volatilizing it with heat. The byproducts are typically gases and liquids from the resin and inorganic material that was present in the composites.

1.2.2.1 Pyrolysis

Pyrolysis, the thermal decomposition of organic molecules in an inert atmosphere

(e.g. N₂), is one of the most widespread recycling processes for FRP. In a pyrolysis process, the first step is to reduce the size of the waste so that it will pyrolyze more easily and fit into the autoclave. Polymeric materials are then heated in the absence of oxygen so that they decompose but do not combust. Combusted matrix products are not usually useful and are similar to those obtained by incineration. The polymeric matrix is volatilized into lower-weight molecules organic substances (liquids and gases), while the fibers remain inert and are eventually recovered. Pyrolysis offers a method of recovering material from the plastic in a scrap composite that has the potential to be used as a feedstock for further chemical processing. The gases evolved are used as fuel to provide heat for the process[4,12-14].

1.2.2.2 Oxidation in fluidized beds

Oxidation is another thermal process for CFRP recycling; it consists in combusting the polymeric matrix in a hot and oxygen-rich flow (e.g. air at 450 °C to 550 °C). This method has been used by a few researchers [15], being the fluidized bed process the most well-known implementation[16-18].

The fiber reinforcement has potentially the most recoverable value in a composite. The theme of research at the University of Nottingham over the past 10 years has therefore been to develop a fluidized bed process to recover high grade glass and carbon fiber reinforcement from scrap glass and carbon fiber reinforced composites. Scrap composites are initially reduced in size to about 25 mm and fed into a fluidized bed. This is a bed of silica sand with a particle size of about 0.85 mm. The sand is fluidized with a stream of hot air and typical fluidizing velocities are 0.4-1.0 m/s at temperatures in the range of 450-550 °C. In the fluidized bed, the plastic volatilizes from the

composite and this releases the fibers and fillers to be carried out of the bed as individual particles suspended in the gas steam. The fibers and fillers are then separated from the gas stream, which can then pass into a high temperature secondary combustion chamber where the plastic is fully oxidized. Energy may subsequently be recovered from these hot combustion products.

1.2.3 Chemical recycling

1.2.3.1 Mixed Acid

Horide et al.[19] developed a FRP recycling method using mixed acid. They can dissolve resin of the epoxy resin system FRP by the mixed acid, ingredient of which is nitric acid and hydrobromic acid (Volume mixing ratio is 2:3). Intensity degradation of the strengthening fiber by the mixed acid processing method was also investigated. By the immersion for 30 minutes, although some strength reduction was seen, intensity was recovered with the increase in immersion time, and the breaking force at the time of 1440-minute progress brought a case where it is not immersed, and a result which increases equally or a little. In the case of glass fiber, it falls gradually.

1.2.3.2 Vegetable oil

Negami et al.[20] developed a new type of heat-dissolution technique in FRP with vegetable oil for recycling. In this method, an easy separation between glass fiber and the matrix resin dissolved was attained. Further, it was found that the FRP dissolution product can be used for a boiler fuel as thermal recycling, and the glass fiber can be used for an asphalt sheet as material.

1.2.3.3 Organic solvent

Iwaya et al.[21] developed a new recycling method using subcritical fluids where unsaturated polyester (UP) resin in FRP can be efficiently depolymerized to separate glass fiber from filler and plastic. Reactions were carried out with or without a catalyst (K₃PO₄) in diethyleneglycol monomethylether (DGMM) and benzyl alcohol under their subcritical state at temperatures 463-623K for 1-8h in a batch reactor. The conversion of UP became fast as the catalyst/solvent molar ratio increased and it was enhanced in the presence of K₃PO₄ catalyst in subcritical benzyl alcohol (BZA). The glass fiber recovered after the FRP treatment in subcritical BZA was relatively long, while it became short and somewhat damaged at temperature higher than 573K.

1.2.3. 4 Subcritical and supercritical fluids process

Supercritical fluids are fluids at temperatures and pressures (typically just) above the critical point; at this stage, the fluid presents itself in one single supercritical phase, while having combined characteristics: liquid-like density and dissolving power, and gas-like viscosity and diffusivity[22]. Supercritical fluids can therefore penetrate porous solids and dissolve organic materials, while still being relatively innocuous under atmospheric conditions[23]. Several types of supercritical fluids (usually coupled with alkali catalysts) have been used for FRP recycling, such as water [24], methanol[25], ethanol[25], acetone[25], and propanol[23,25-26]. Chemical recycling with supercritical fluids is a more recent approach; it is nevertheless already recognized for producing recycled fibers with virtually no mechanical degradation, especially when using propanol, and for allowing recovering useful chemicals from the matrix.

1.3 Reusing technologies of recycled materials

1.3.1 Reuse of recycled plastic

Materials recycled from FRP include fiber and plastic. The recycled plastic was usually reused as fuel[8-11]. In some cases, plastic broke down into lower molecular weight organic substances. It is difficult to reuse as plastic for FRP, so it was reused as fuel to recycle energy. Although plastic recycled from FRP that has the potential to be used as a feedstock for further chemical processing, resynthesis is costly and hard to put into practice. Up to now, the recycled plastic was reused as fuel, and there was scarce research to develop a technology to reuse recycled plastic efficiently.

1.3.2 Reuse of recycled fiber

Fibrous recyclates obtained through above technologies were either short or fluffy. Therefore, the existing manufacturing processes, developed for virgin materials, typically available as sized tows, must be adapted to the unique recycled-fiber form. Re-manufacturing processes adapted to the unique recycled-fiber are listed as follows.

1.3.2.1 Filler for concrete and cement composites

Asokan et al.[10-11] did their efforts to recycle glass fiber reinforced plastic (GFRP) waste powder and fiber in concrete and cement composites and assess its quality to comply with the British standards for use in construction applications. Although the 28 days compressive strength was not higher than the standard structural concrete values, i.e. 45N/mm², the findings of this preliminary study showed a viable technological option for the use of GFRP waste in precast concrete products such as precast paving slabs, roof tiles, precast concrete wall elements, lightweight concrete, concrete paving

blocks and architectural cladding materials. The properties of panel products depend on the consistency and quality of GRP waste fiber, and access to specialized architectural cladding manufacturing facilities.

1.3.2.2 Injection molding

During Injection molding, a mixture of resin (typically a thermoplastic), recycled fibers (short or milled) and fillers/additives is pre-compounded into pellets, which are subsequently injected into a mold.

Takahashi et al.[27] injected recycled carbon fiber with polypropylene (PP). A directional difference in mechanical properties by using the injection molded plates to understand an actual performance of injection molded automotive parts was investigated.

1.3.2.3 Bulk molding compound (BMC) compression

BMCs are intermediate products made by mixing resin (typically a thermoset), recycled, fillers and curing agents into bulky charges; this premix is subsequently compression molded into a component.

Pickering et al.[28] and Turner et al.[29] molded several BMCs with recycled carbon fibers. The main factors affecting the mechanical performance of the recycled CFRPs (especially the strength) were the fractions of fillers and of recycled carbon fibers. The mechanical performance of the recycled CFRPs was superior to that of commercial glass BMCs.

1.3.2.4 Intermediate non-woven products

The production and subsequent re-impregnation of 2D or 3D recycled fiber non-woven dry products (with a short and random reinforcement architecture) is one of the most widely used manufacturing processes for recycled FRPs.

Szpieg et al.[30] produced recycled FRP composite use recycled PP which was reprocessed into a film and recycled fiber. The fiber preforms and PP films were stacked and composite materials were subsequently manufactured by press forming. The mechanical behavior of fiber preforms was characterized by a compaction test and compared to the results obtained by consolidation test of the fiber reinforced PP composites.

1.3.2.5 Fiber alignment

Fiber alignment is a key point to improve the mechanical performance of composites manufactured with discontinuous recycled fibers: not only the composite's mechanical properties improve along preferential fiber direction, as manufacturing requires lower molding pressures and smoother fiber-to-fiber interactions[29,31].

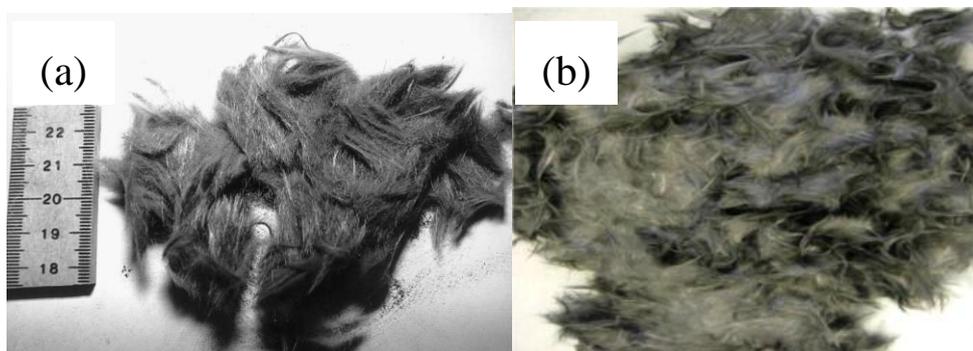
1.3.2.6 Woven recycled FRP

As some recycling processes can preserve the reinforcement architecture of the waste, it is possible to recover the structured weave from large woven items, e.g. out-of-date pre-preg rolls, end of life aircraft fuselage, or pre-preg trimmings from large components; re-impregnating (through e.g. resin transfer molding (RTM) or resin infusion) the recycled weave fabrics then produces woven recycled FRPs.

1.4 Constitution of this dissertation

From above mentioned recycling technologies (mechanical recycling, thermal processing and chemical recycling), fibers could be recycled by all these method. However, they are not fully satisfactory: Mechanical recycling leads to fillers/short fibers mixtures, with poor reinforcing properties. Thermal processing is conducted under high temperature, so clean fibers are produced with a lost in the mechanical properties of the fibers. Chemical recycling is a new and promising route for converting plastic wastes by returning them back to their original constituents, that is, monomers or petrochemical feedstock, and has received a great deal of attention in recent years[32-34]. But chemical processing is very costly, for both expensive equipment and chemical agent. One other problem is recycling of chemical agent.

It is should be concerned that the recycled fibers are usually fragmented into short lengths, as a result of (i) size-reduction of FRP waste before reclamation, (ii) fiber breakage during reclamation, and (iii) chopping of the fibers after reclamation. In addition, all fiber reclamation processes remove the sizing from the fibers, so the recycle is in a filamented, random, low-density-packing (fluffy) form(Fig.1).



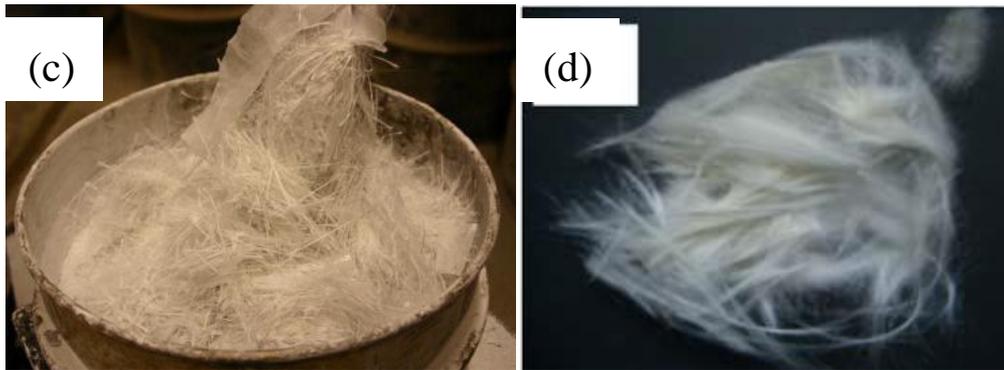


Fig.1-1 Recycled fibers in a typical unsized, random, low-density-packing (fluffy) form(a)[16] (b)[35](c)[10](d)[21]

Higher fiber lengths have greater intrinsic value further down the fiber lifecycle due to their ability to achieve higher mechanical properties in molded parts[36]. The longer the recycled fibers are, the more orderly the recycled fibers are, and the more valuable the recycled fibers are. Kemmochi et al.[37] reported that reinforced fibers do not deteriorate under accelerated aging experiment, which corresponds to 10 years. It could be considered that fibers which inside FRP is the same as virgin fiber. So we put our eye on the value fiber. Fiber is very expensive, carbon fiber is about 10 thousand yen/kg and glass fiber is about 750 yen/Kg. In this research, we are interested in these expensive fibers. In other words, we investigated recycled fiber reused in low cost and high value with low damage even if no damage. If we can recycle fiber without a lost in the mechanical properties, the value of recycled fiber will greater than cost of recycling. It will realize sustainable recycling without support of government. Besides, we can reduce the environment impact in the future.

In order to reduce the fiber breakage during reclamation and enhance the value of recycled fiber, a new recycling technology using a steam system, which is a kind of pyrolysis belong to thermal processing , has been developed. As mentioned above, in a

pyrolysis process, the first step is to reduce the size of the waste so that it will pyrolyze more easily and fit into the autoclave. Polymeric materials are then heated in the absence of oxygen. Thermal processing is conducted under high temperature, so clean fibers are produced with a loss in the mechanical properties of the fibers. In this research, size of waste FRP needn't to reduce, so long fiber can be collected after decomposition process. The size of waste FRP is only enslaved to size of heating chamber of equipment. Besides, we investigated the effect of pyrolysis time and temperature on the mechanical properties of recycled fiber, based on tensile strength measurements, determining the optimum decomposition conditions for FRP by superheated steam. So the polymeric matrix is volatilized into lower-weight molecules organic substances under a lowest limit of temperature, the fiber recycled without a loss in the mechanical properties. In short, we develop a recycling method to recycle long fiber with low damage even if no damage. The value of fiber was recycled furthest. The experimental processes and results will be summarized in Chapter 2.

Although resin is recoverable, since it deteriorated in years of use, the polymeric matrix is volatilized into lower-weight molecules organic substances in a pyrolysis process. It is difficult to reuse as resin by re-polymerization. So we propose that it can be reused as fuel. The bomb calorimeter was the most common device for measuring the heat of combustion or calorific value of a material. The calorific value of recycled pyrolysis oil was measured by bomb calorimeter. Calorific value of recycled pyrolysis oil was a little lower than that of diesel, petrol and kerosene, higher than wood (15% water), the same as steam coal (1% water). It was possible to use recycled pyrolysis oil as a fuel in the further. The details of above contents will be discussed in Chapter 3.

Because FRPs were pyrolyzed under a lowest limit of temperature, fibers with clean

surface can't be produced. Recycled fibers were surface treated for reuse as FRP composites. A low cost and simple surface cleaning method was developed for surface treatment. Recycled glass fibers and carbon fibers were treated using acetone and N-Methyl-2-pyrrolidinone (NMP) respectively. Most residual resin impurities were removed by surface treatment. Analysis indicated no adverse effect of surface treatment on bending strength. The mechanical properties of the treated recycled glass fiber reinforced plastic (TR-GFRP) and treated recycled carbon fiber reinforced plastic (TR-CFRP) composites were determined and compared with those of recycled glass fiber reinforced plastic (R-GFRP) and recycled carbon fiber reinforced plastic (R-CFRP). The bending strengths of R-GFRP and R-CFRP were very low, compared to that of virgin glass fiber-reinforced plastic (V-GFRP) and that of virgin carbon fiber-reinforced plastic (V-CFRP). The bending strength of TR-GFRP composites was improved to about 90% of that of V-GFRP, and the bending strength of TR-CFRP composites was improved to about 80% of that of V-CFRP. The experimental processes and results will be summarized in Chapter 4.

Since dynamic power may be received in further application of recycled FRP, the influence of recycling on the impact damage resistance of recycled FRP composites was investigated using low-velocity impact and compression after impact (CAI) tests. The relationships among load, force, and time were analyzed to gain insight into the damage characteristics of three types of composite laminate: virgin FRP, recycled FRP, and treated recycled FRP. Special emphasis was placed on evaluating the extent of damage and the residual mechanical properties as affected by three different fiber surface states. Substantial differences were noted in the shape, area, and damage mode of impact using ultrasonic c-scanning, photography, and scanning electron microscopy (SEM). Virgin

FRP indicated significant improvement in impact damage resistance in the form of less damage, higher residual strength, and greater shear failure angle. Damage resistance was improved up to 80% of V-CFRP by surface cleaning while R-CFRP is 50% of V-CFRP. Shear failure angle of 16° was attained from R-CFRP and it was increased to 24° when the recycled fibers were cleaned. The result of SEM showed that there was less delamination of TR-CFRP compared with R-CFRP. This work proves that the low-velocity impact response of recycled composites can rival that of virgin composites, while providing a basis for future applications of recycled carbon in many fields. The detail discussions and results will be reported in Chapter 5.

In chapter 6, I did a brief conclusion of this dissertation.

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CHAPTER TWO

Pyrolysis of fiber reinforced plastic

Chapter2 Pyrolysis of fiber reinforced plastic

2.1 Introduction

As the worldwide amount of fiber used for FRP composite materials grows, there is concern about the potential tonnage of waste from manufacturing processes and end of life products. The waste related to fiber products will quickly reach a significant level to become an important environmental issue since such products are not biodegradable[1]. In addition, the raw fiber is extremely expensive, especially carbon fiber, because of the high consumption of energy in its manufacture[2]. Such a high consumption of energy also discourages their use from the perspective of green chemistry; therefore, manufacturers will need to identify ways to comply with legislation on sustainability[3-4]. Therefore, the recycling of FRP composite materials will contribute to the sustainability and sustainable development of industrial processes. In recent years, there is a strong interest in developing processes for reusing and recycling of reinforced fiber from waste FRP materials.

Since the early 90s of 20th century, studies on recycling of fiber reinforced resin composites could be classified into three types[5]: mechanical recycling [6-8], thermal processes [9-16] and chemical recycling [17-35].

Mechanical recycling as an original mean produces powdered fillers and fiber products. Kouparitsas et al.[7] and Palmer et al.[8] grinded the composites to achieve fillers or/and fibers of wide-ranged lengths. Mechanical treatment produces fillers or short-fibers that can only be reused as reinforcing materials. By this process, the composites had been recycled, although long and high valuable fibers could not be obtained.

Pyrolysis and oxidation processes in a fluidized bed, as common thermal process, are conducted at high temperature. Pyrolysis process gives chemical products, clean fibers and fillers. Plastic is volatilized into lower-weight molecules organic substances during the process, non-fiber material can be only claimed by means of the energy recovery. Torres et al.[9] recycled the composites by pyrolyzing over 400°C and obtained a complex liquid mixture of C₅-C₂₀ organic compounds that could be used as fuel oils. Clean fibers are produced at these operating conditions but at expense of a lost in the mechanical properties of the fibers. Fluidized bed process as another thermal process can produce clean fibers and fillers with energy recovery. Pickering et al.[12-15] successfully recycled glass fibers by fluidized-bed process from composites at a bed temperature of 450°C and a fluidizing velocity of 1.3 m/s. And later Zheng et al.[16] recycled glass fibers from the printed circuit boards at the temperature ranging from 400°C to 600°C. The fluidized bed process really gives clean fibers and other products but the reclaimed fibers would be highly oxidized, causing property reduction.

The supercritical fluids, one kind of chemical recycling, which have the combined characteristics of liquid-like density, dissolving power, gas-like viscosity and diffusivity have been used to recycle the composites. More recently, Bai et al.[36] recycled carbon fibers from CFRP in supercritical water in the presence of oxygen. They found that oxygen can promote the decomposition of epoxy resin. However, the tensile strength of the recovered carbon fibers decreased rapidly when the decomposition efficiency of polymer matrix was increased to 96.5 wt% above, which was attributed to the excessive oxidation of recovered carbon fibers. Compared to the mechanical and thermal processes mentioned above, chemical recycling is not effective to recycle the composites because not all the solution is feasible to all composites. Developing method

for chemical recycling of thermoset composites to useful fibers and organic compounds is also an important issue. Chemical process is very costly, for both expensive equipment and chemical agent. One other problem is recycling of chemical agent.

The production of reinforced fiber is a high cost process in energy. If reinforced fiber with high properties is recycled in an economical way, the recovered reinforced fiber can displace pristine counterparts in some applications. As a result, a lot of energy for producing reinforced fiber will be saved. Kemmochi et al.[37] reported that reinforced fibers do not deteriorate under accelerated aging experiment, which corresponds to 10 years. It could be considered that fibers which inside FRP is the same as virgin fiber. In this research, we are interested in these expensive fibers. In other words, we investigated recycled fiber reused in low cost and high value with low damage even if no damage. If we can recycle fiber without a lost in the mechanical properties, the value of recycled fiber will greater than cost of recycling. It will realize sustainable recycling without support of government. Besides, we can reduce the environment impact in the future.

The most valuable of which are long and high modulus fibers. Milled fiber products are readily available and have little intrinsic value. In order to enhance the value of recycled fiber, we developed a new recycling technology using a steam system to recycle long and high mechanical property fibers. In chapter 2, FRP was efficiently degraded, and reinforced fiber was separated from resin by superheated steam. The influence of pyrolysis temperature and time on the mechanical properties of recycled fiber was investigated, and optimum pyrolysis conditions for FRP by superheated steam were identified. The mechanism of pyrolysis was also elucidated.

2.2 Superheated steam

Our previous studies[38] have demonstrated that it is possible to decompose FRP into reinforced fiber and resin by superheated steam, which is to steam at a temperature above water's boiling point. If saturated steam is heated under a constant pressure, its temperature rises and it starts producing superheated steam. The characteristics of superheated steam are: (1) higher temperature than that of saturated vapor; (2) greater specific volume than that of saturated vapor; (3) higher energy than saturated vapor's enthalpy. Superheated steam provides advantages over air-processing mediums including increased heat transferring that may improve thermal degradation and provide an oxygen-free environment.

2.3 Pyrolysis of GFRP

2.3.1 Experimental methods

2.3.1.1 GFRP samples manufacture

Commercially available unsaturated glass fibers with a diameter of 16 to 18 μm , purchased from Unitika, were used as reinforcement fiber in the present work. Unsaturated polyester resin was obtained from Showa Highpolymer, and epoxy resin was obtained from Nagase ChemteX. Pamekku N was chosen as the hardener and was purchased from Nof. Unsaturated polyester resin/hardener were 100 and 0.8 parts by weight. Epoxy resin/ hardener were 100 and 27 parts by weight. The prepreg was fabricated by vacuum-aided resin-transfer molding (VARTM). These materials are listed in Table 2-1. The GFRP was cut into scrap ($50 \times 200 \text{ mm}^2$) after hardened.

Table 2-1. Raw materials for specimens

Resin	Hardener	Fiber
Unsaturated polyester resin (Showa Highpolymer)	Pamekku N (Nof)	Unidirectional glass fiber (Unitika)
Epoxy resin XNR6815(Nagase ChemteX)	XNH6815 (Nagase ChemteX)	Unidirectional glass fiber (Unitika)

2.3.1.2 Pyrolysis by superheated steam

2.3.1.2.1 Resin

The two kinds of resin (unsaturated polyester resin and epoxy resin) were molded into a cuboid of 38×32×12 mm³. After hardened, resin was fed into a drying oven at 50°C for 60 min. The weight was immediately recorded by electronic balance. The resin samples were first fed into a vat and then fed into the chamber and heated for a predetermined time at different temperatures. The weights of the remaining char and the vat were recorded by an electronic balance after drying. The yield, remainder (wt%) was calculated as:

$$Yield, remainder = \frac{W_3 - W_2}{W_1} \times 100\% \quad (1)$$

i.e. here W_1 is the weight of untreated resin, W_2 is the weight of the vat, and W_3 is the weight of the remainder.

2.3.1.2.2 GFRP

GFRP samples were fed into the chamber. In the chamber, the GFRP was heated in the absence of oxygen and kept under different temperatures for a predetermined time, or under a predetermined temperature for different amounts of time, in superheated steam (Table 2-2). An instrument with superheated steam was depicted in Fig. 2-1. After the experiment, FRP samples were cooled to room temperature.

Table 2-2. Pyrolysis conditions of GFRP

Resin	Decomposition		Decomposition time					
	temperature (°C)		(min)					
Unsaturated polyester	370	30	60	120	180	240	300	
	450	5	30	60	90	150	—	
Epoxy	340	30	60	120	180	240	300	
	450	5	30	60	90	150	—	

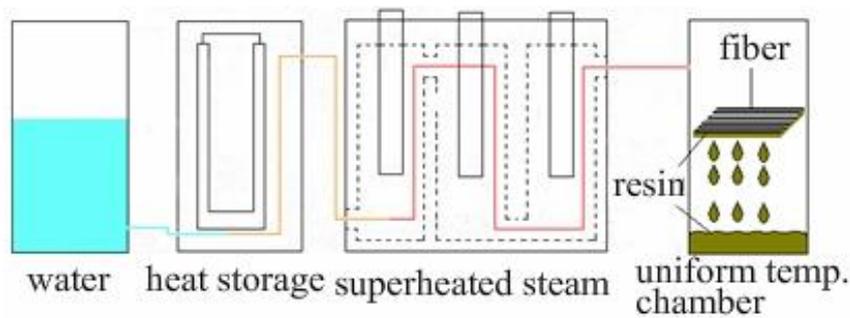


Fig.2-1 Schematic view of the superheated steam recycling instrument.

2.3.1.3 Glass fiber heated in different environments

The tensile strength of recycled fibers was obviously degraded in the previous work[38]. In order to investigate reasons for the degradation of recycled fiber tensile strength, glass fibers were heated in different environments (air atmosphere, inert atmosphere, and superheated steam atmosphere). For air atmosphere heating, sample-1 (virgin glass fibers) was heated by a muffle furnace. For inert atmosphere heating (Fig. 2-2), virgin glass fibers were placed into a glass tube that was sealed at one end by a high temperature burner, and then the air was sucked out of the glass tube by a vacuum pump. In step I, A was switched off, B was switched on, and the tube was filled with argon gas. In step II, B was switched off, A was switched on, and mixed air was sucked

out of the tube. Steps I and II were repeated five times, and the glass fibers were surrounded by pure argon gas in the glass tube. Sample-2 (Fig. 2-3) was completed by sealing off the other end of the tube using a high temperature burner. Sample-2 was heated by a muffle furnace. For superheated steam atmosphere heating, sample-3 (virgin glass fibers) was heated by superheated steam equipment.

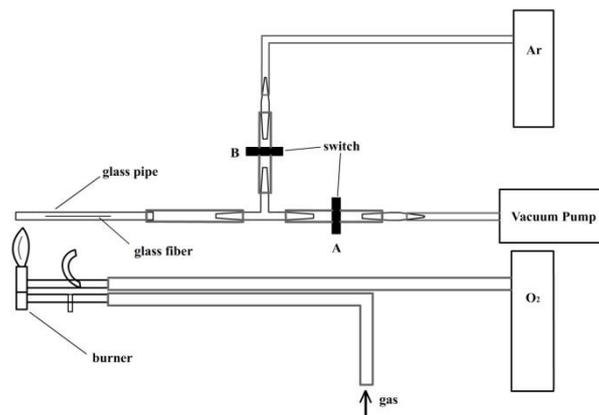


Fig. 2-2 Schematic drawing of prepared sample-2, which was heated in inert atmosphere



Fig. 2-3 Picture of sample-2

2.3.1.4 Scanning electron microscopy

Samples of recycled and virgin fibers were analyzed by using scanning electron microscopy (SEM Hitachi S-3000N) to determine the morphology and diameter of the fibers, as well as visual signs of residual resin impurities. Fibers were mounted on carbon discs and gold-coated to a thickness of 13 Å. The microscope was then operated in high-vacuum mode, and images were obtained through a secondary electron detector.

2.3.1.5 Mechanical strength test

The tensile strength of the recycled fiber was determined according to the standard method JIS R3420. The test machine, auto graph (Shimazu AG-20KND) fitted with a load cell (SFL-20KNAG), was used.

2.3.2 Results and discussion

2.3.2.1 Pyrolysis by superheated steam

2.3.2.1.1 Resin

Eight sets of samples were prepared for the pyrolysis of resin as mentioned in section 2.3.1.2.1. One set comprised a piece of unsaturated polyester resin sample and a piece of epoxy resin sample. Each set of samples was fed into a chamber and heated for 30 minutes at a predetermined temperature (listed in Table 2-3).

Table 2-3. Pyrolysis conditions of resin

No.	Decomposition time (min)	Decomposition temperature (°C)
1	30	230
2	30	250
3	30	280
4	30	310
5	30	340
6	30	370
7	30	400
8	30	430

The yield, obtained by eq. (1), was summarized in Fig. 2-4. Results indicated that the beginning point of depolymerization of epoxy resin was lower than that of unsaturated polyester resin. Likewise, the ending point of depolymerization of epoxy resin was

lower than that of unsaturated polyester resin. The discrepancy was 30°C. Both residue rates of resin were below 20% at the end of decomposition.

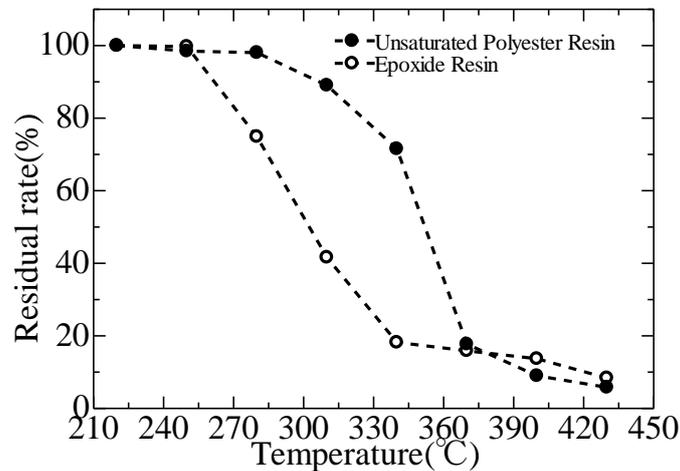


Fig. 2-4. Residue rate of decomposed resin.

2.3.2.1.2 GFRP

Pyrolysis was carried out at different times at 340, 370, and 450°C. These temperatures were chosen based on the results presented in section 2.3.2.1.1. In the pyrolysis process, the GFRP was heated in the absence of oxygen. Under these conditions, resin breaks down into lower molecular weight organic substances (gases); there was also a solid carbon char product. The recycled fibers were orderly and had the potential to be used as a feedstock for further GFRP processing.

2.3.2.2 Surface morphology

The reclaimed fibers were analyzed by SEM. All the SEM micrographs of the reclaimed glass fibers in Fig. 2-5 and 2-6 were from GFRP (left column, reclaimed fibers at 250× magnification; right column, close-up view of a single glass fiber at 5,000× magnification). In low magnification micrographs (250×), we were able to

observe the char that remained on glass fibers. In high magnification micrographs (5000×), we were able to scrutinize the damage of glass fibers.

The pictures in Fig. 2-5 (a) were SEM micrographs of recycled glass fibers, which were reclaimed at a temperature of 340°C for 60 min. Likewise, those of Fig. 2-5 (c) were reclaimed at a temperature of 450°C for 5 min. Those of Fig. 2-6 (e) were reclaimed at a temperature of 370°C for 60 min. Those of Fig. 2-6 (g) were reclaimed at a temperature of 450°C for 5 min. In the low magnification micrographs [Fig. 2-5 (a), Fig. 2-5 (c), Fig. 2-6 (e), and Fig. 2-6 (g)], more char impurities remained on the fiber's surface after superheated steam treatment than on virgin fibers (Fig. 2-7). In low magnification micrographs [Fig. 2-5 (a) and Fig. 2-6 (e)], more char impurities could be observed than in Fig. 2-5 (c) and Fig. 2-6 (g). These observations indicated that char impurities would decrease with increasing temperature. The pictures presented in Fig. 2-5 (b) were SEM micrographs of recycled glass fibers reclaimed at a temperature of 340°C for 300 min. Likewise, those of Fig. 2-5 (d) were reclaimed at a temperature of 450°C for 150 min. Those of Fig. 2-6 (f) were reclaimed at a temperature of 370°C for 300 min. Those of Fig. 2-6 (h) were reclaimed at a temperature of 450°C for 150 min. In the low magnification micrographs [Fig. 2-5 (b), Fig. 2-5 (d), Fig. 2-6 (f), and Fig. 2-6 (h)], the fiber's surface was almost char-free. For the same decomposition temperature and different decomposition times [e.g., low magnification micrographs Fig. 2-5 (a) and Fig. 2-5 (b)], more char impurities remained on fibers in micrograph Fig. 2-5 (a) than in micrograph Fig. 2-5 (b). Char impurities could have been reduced by the increase in decomposition time. In addition, no physical damage (e.g., fissures or cracks) or morphological changes (e.g., diameter or surface roughness) were observed in any SEM micrograph of 5000×.

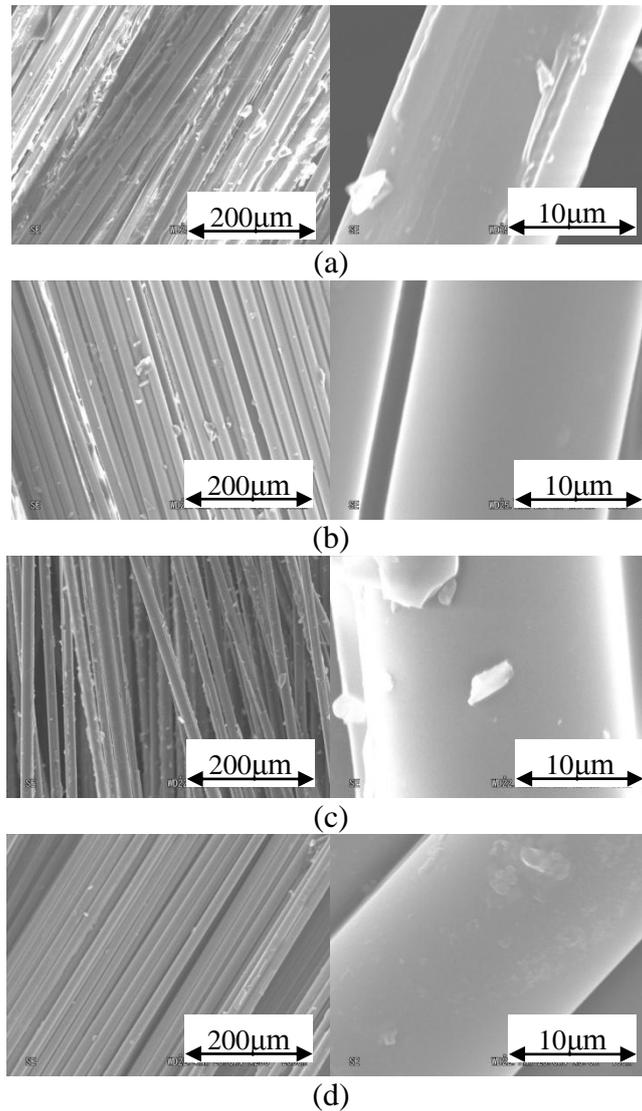


Fig.2-5 SEM micrographs of recycled fibers from pyrolysis of epoxy glass fiber composite under different decomposition conditions. (a) reclaimed at a temperature of 340°C for 60 min (b) reclaimed at a temperature of 340°C for 300 min (c) reclaimed at a temperature of 450°C for 5 min (d) reclaimed at a temperature of 450°C for 150 min

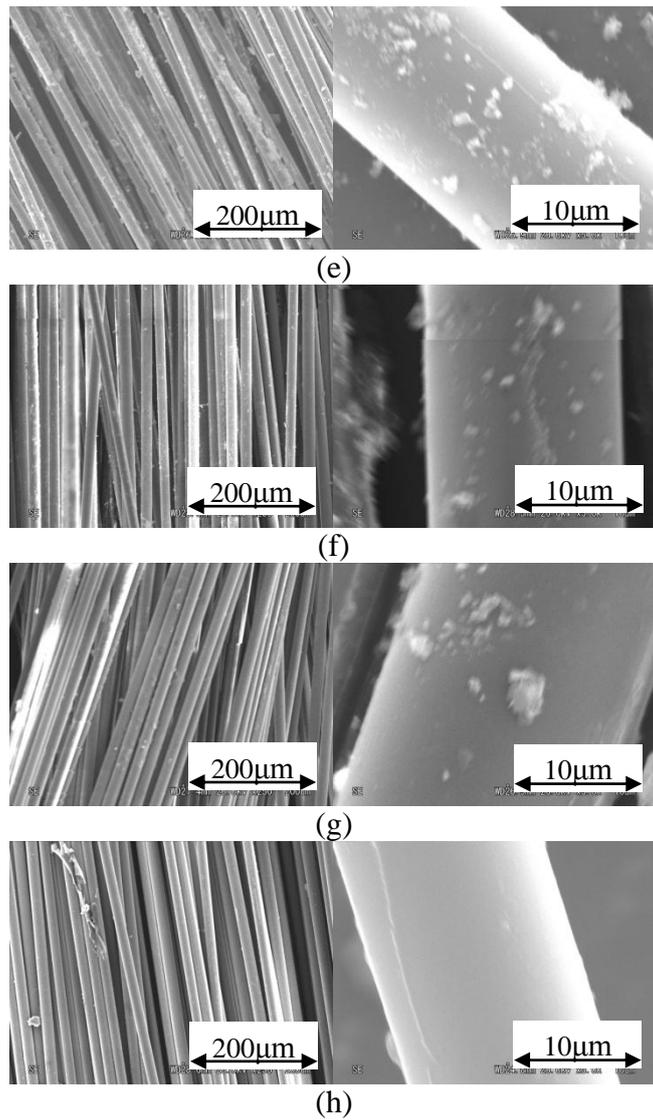


Fig.2-6 SEM micrographs of recycled fibers from pyrolysis of unsaturated polyester glass fiber composite under different decomposition conditions. (e) reclaimed at a temperature of 370°C for 60 min (f) reclaimed at a temperature of 370°C for 300 min (g) reclaimed at a temperature of 450°C for 5 min (h) reclaimed at a temperature of 450°C for 150 min

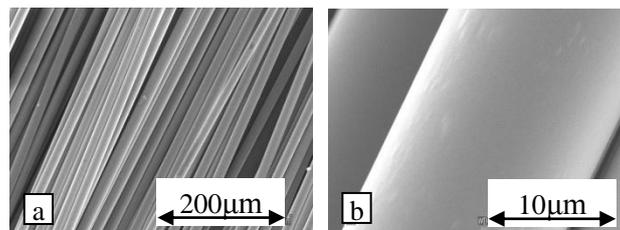


Fig. 2-7. SEM micrographs of virgin glass fiber at (a) 250× and (b) 5,000× magnifications.

2.3.2.3 Virgin glass fiber heated under different atmospheres

Figure 2-8 plots tensile strength vs. heating temperature of heated virgin glass fibers. The horizontal axis is the heating temperature, and the ordinate axis is the tensile strength of glass fibers. The horizontal line denotes the tensile strength of unheated glass fibers. The circle shape denotes the tensile strength of glass fibers heated in a superheated steam atmosphere, the triangular shape denotes that of glass fibers heated in inert atmosphere, and the square shape denotes that of glass fibers heated in air atmosphere. The tensile strength of glass fibers degenerated beginning at 100°C. Nearly the same variation was observed among the three kinds of glass fibers heated in different atmospheres. Over 50% decrease was observed at 400°C. Three different superheated steam atmospheres were analyzed: steam (H₂O), absence of oxygen, and high temperature. The inert atmosphere could be considered as two kinds of parameters: absence of oxygen and high temperature. Two different air atmospheres were analyzed: oxygen and high temperature. From the results of superheated steam atmosphere and inert atmosphere, we can infer that steam is not a crucial parameter that influences tensile strength. Likewise, from the results of inert atmosphere and air atmosphere, we can infer that oxygen is not a crucial parameter. Temperature is the crucial parameter that influences tensile strength. It is assumed that the tensile strength of glass fibers is reduced with increased heating temperature. These results imply that setting the temperature of pyrolysis as low as possible to obtain high-value recycled glass fibers is significant when reclaiming GFRP.

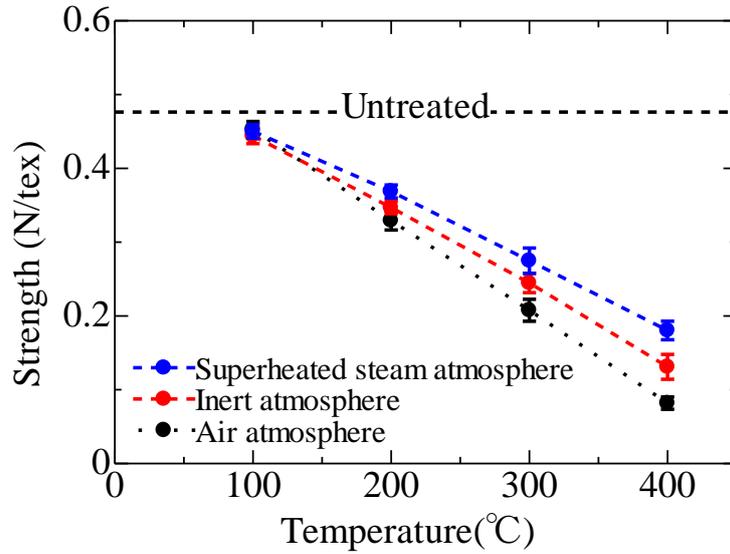


Fig. 2-8 Variation in tensile strength of virgin glass fibers with increasing temperature in different atmospheres

2.3.2.4 Mechanical properties of the recovered fibers

The tensile strength vs pyrolysis temperature of recycled fibers was plotted in Fig. 2-9. The tensile strengths of fiber recycled at 340 and 370°C were the same as that of virgin fiber. Under these conditions, the fiber's tensile strength was not reduced. This was attributed to the fact that resin protected the glass fibers and thus prevented the temperature from affecting the glass fiber strength. At higher temperatures, there was significantly greater reduction in mechanical strength (e.g., 60% reduction at 450°C). Under this condition, the resin volatilized from GFRP, and the glass fiber was exposed to superheated steam. Thus, the glass fibers were immediately exposed to high temperature with no protective layer. The results obtained from the mechanical characterization of the fibers were considerably better than those obtained from alternative processes (e.g., fluidized bed and microwave-assisted techniques, which reduce the fiber strength by 50%) [13,39].

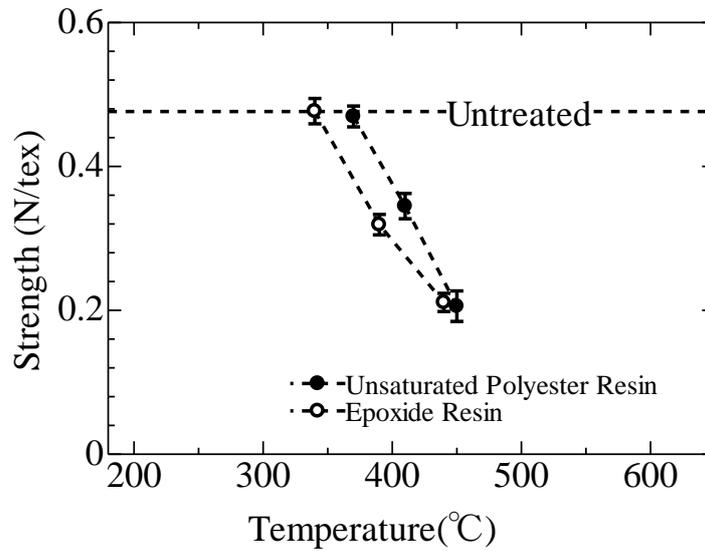


Fig.2-9 Tensile strength vs. pyrolysis temperature curve of recycled fibers, processed for 30 minutes. Solid circle denotes reclaimed fibers from pyrolysis of unsaturated polyester GFRP; hollow circle denotes recycled fiber from pyrolysis of epoxy GFRP.

2.3.2.5 Optimum decomposition conditions

2.3.2.5.1 Unsaturated polyester GFRP

Figures 2-10 and 2-11 plotted the tensile strength vs pyrolysis time curve of recycled fibers reclaimed by decomposing unsaturated polyester GFRP at a constant temperature. The horizontal axis represented decomposition time, and the vertical axis represented tensile strength. The strength of the recycled glass fiber was lower than that of the virgin fiber. With a decomposition time of 30 min and a decomposition temperature of 370°C, the fiber tensile strength was scarcely reduced and was the same as that of virgin fiber. With a pyrolysis time exceeding 30 min and a pyrolysis temperature of 450°C, the tensile strength was almost steady after 30 min. These results indicated that the tensile strength of unsaturated polyester GFRP glass fibers heated under pyrolysis condition of 370°C for 30 min was only slightly degraded.

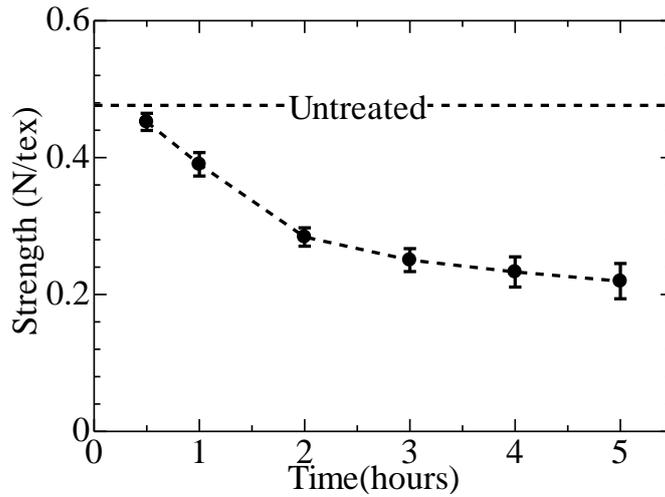


Fig.2-10. Tensile strength vs. pyrolysis time curve of recycled fibers reclaimed by decomposing unsaturated polyester GFRP at 370°C.

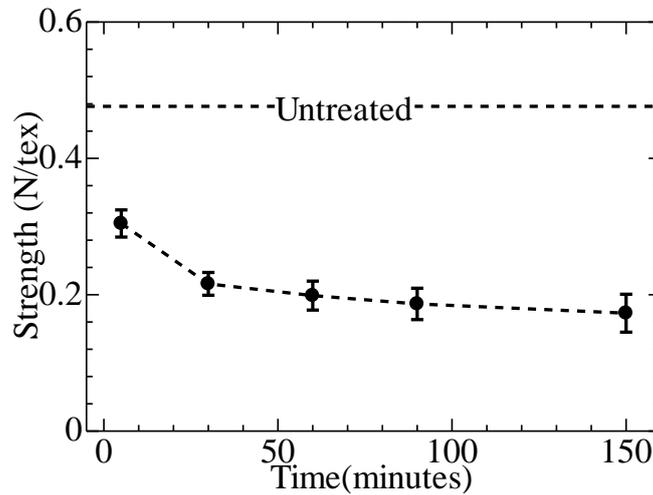


Fig. 2-11. Tensile strength vs. pyrolysis time curve of recycled fibers reclaimed by decomposing unsaturated polyester GFRP at 450°C.

2.3.2.5.2 Epoxy GFRP

Figures 2-12 and 2-13 plotted the tensile strength vs pyrolysis time curve of recycled fibers reclaimed by decomposing epoxy GFRP at a constant temperature. A decomposition time of 30 min and a decomposition temperature of 340°C hardly reduced the fiber tensile strength, compared to virgin fiber. In Fig. 8, the tensile strength of recycled fiber degraded for 30 min and was lower than that in Fig. 2-9, probably due

to the earlier loss of resin protection than in Fig. 6, since epoxy resin decomposed earlier than unsaturated polyester. Epoxy GFRP degraded under pyrolysis condition of 340°C for 30 min exhibited little deterioration of the tensile strength.

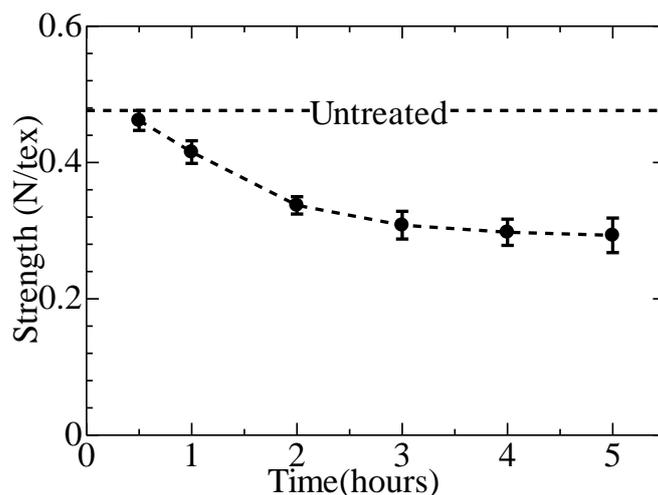


Fig. 2-12 Tensile strength vs. pyrolysis time curve of recycled fibers reclaimed by decomposing epoxy GFRP at 340°C.

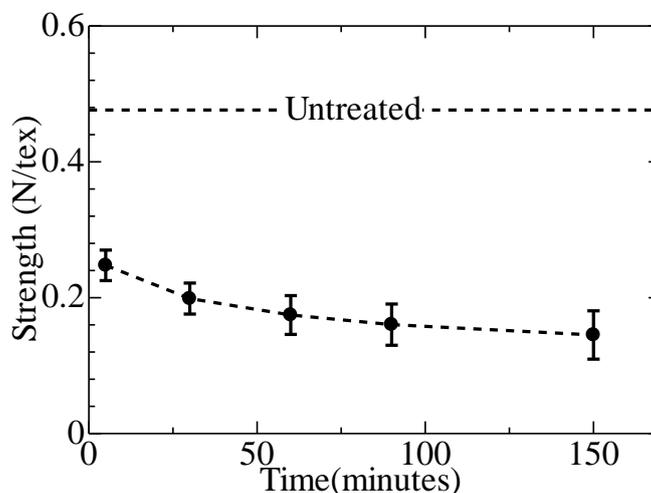


Fig. 2-13. Tensile strength vs. pyrolysis time curve of recycled fibers reclaimed by decomposing epoxy GFRP at 450°C.

In reusing recycled glass fiber for manufacturing GFRP, the tensile strength of recycled fiber was a yardstick for evaluating the conditions under which the GFRP was decomposed. Pyrolysis at 370°C for 30 min produced the highest tensile strength of

recycled fiber, close to that of virgin fiber. Therefore, these conditions were optimal for unsaturated polyester GFRP in this study. Furthermore, pyrolysis at 340°C for 30 min yielded the highest tensile strength of recycled fiber, approaching that of virgin fiber. Thus, these were the optimal conditions for epoxy GFRP in this study.

The curve of the residual rate of unsaturated polyester resin (Fig. 2-4) indicated that hardly any unsaturated polyester resin remained in vat at 370°C (take unsaturated polyester GFRP as an example). The residual rate of unsaturated polyester resin declined as the pyrolysis temperature increased. Resin protected the glass fibers and prevented the temperature from affecting the fiber strength until the residual rate of unsaturated polyester resin was reduced to 20% at 370°C. When the residual rate of unsaturated polyester resin was below 20%, fiber was exposed to superheated steam without any protective layer, resulting in a diminution of fiber tensile strength. In other words, under conditions for which the resin was about to decompose completely, the tensile strength of recycled fiber approached that of virgin fiber.

2.4 Pyrolysis of CFRP

2.4.1 Experimental and methods

2.4.1.1 CFRP samples manufacture

Commercially available woven carbon fibers (CO6343) purchased from Toray, were used as reinforcement fiber in the present work. Epoxy resin was obtained from Nagase ChemteX. Epoxy resin (XNR6815)/hardener (XNH6815) were 100 and 27 parts by weight. The prepreg was fabricated by vacuum aided resin transfer molding (VARTM). The CFRP were cut into scrap ($25 \times 200 \text{ mm}^2$) after hardened.

2.4.1.2 Pyrolysis by superheated steam

CFRP samples were fed into the chamber. In the chamber, the CFRP were heated in the absence of oxygen and kept under different temperatures for a predetermined time, or under a predetermined temperature for different amounts of time, in superheated steam (Table 2-4). After the experiment, samples were cooled to room temperature.

Table 2-4 Pyrolysis conditions

Resin	Temperature	Time			
	(°C)	(min)	(min)	(min)	(min)
Epoxy	340	15	30	60	90
	390	—	30	—	—
	440	—	30	—	—

2.4.1.3 Virgin carbon fibers heated under different environment

It is obviously showed that tensile strength of recycled fibers is degraded in the previous work[38]. In order to investigate reason which lead the decline of recycled fibers on tensile strength, carbon fibers were heated under different environment (air atmosphere, inert atmosphere and superheated steam atmosphere). Air atmosphere heating: Sample-1(virgin carbon fibers) was heated by muffle furnace. Inert atmosphere heating (Fig.2-14): Virgin carbon fibers were put into a glass tube which sealed off one end by high temperature burner, then sucked the air out of the glass tube by a vacuum pump. Step I: Switch off A and switch on B, argon gas poured into the glass tube. Step II: Switch off B and switch on A, mixed air was sucked out of tube. Do step I and II repeatedly (5 times), carbon fibers were surrounded by pure argon gas in glass tube. Sample-2(Fig.2-15) was completed by sealing off the other end of tube use high temperature burner. Sample-2 was heated by muffle furnace. Superheated steam

atmosphere heating: Sample-3(virgin carbon fibers) was heated by superheated steam equipment.

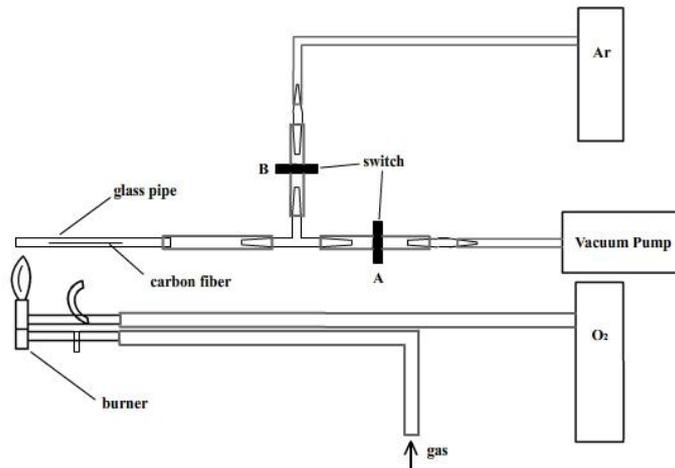


Fig.2-14 Schematic drawing of preparing sample-2 which heated under inert atmosphere



Fig. 2-15 Picture of sample-2

2.4.1.4 SEM

Samples of recycled (obtained from section 2.4.1.2) and virgin (obtained from section 2.4.1.3) fibers were analyzed by using scanning electron microscopy (SEM; Hitachi S-3000N) to determine the morphology and diameter of the fibers, as well as visual signs of residual resin impurities.

2.4.1.5 Mechanical strength test

If the recycled carbon fibers could fully exploit the mechanical performance, and reused in some fields of low mechanical properties requirement as substitute of virgin

carbon fibers, it will save large amounts of energy and production cost. Current estimates suggest that reclaiming recycled carbon fibers requires only a small fraction of the resources for producing virgin carbon fibers (Table 2-5), so recycling CFRP appears to be economically and environmentally viable.

Table 2-5 Comparing the cost of virgin carbon fibers and recycled carbon fibers[40]

Fiber type	Cost to manufacture	
	Materials price US\$/kg	Energy kWh/kg
Virgin carbon fibers	33-66	55-165
Recycled carbon fibers	17-26	3-10

For the purpose of reveal the influence of different parameters (temperature and time) on the pyrolysis of CFRP, the tensile strength of the recycled fiber was determined by strength tester. The test machine, auto graph (Shimadzu AG-20KND) fitted with a load cell (SFL-20KNAG), was used.

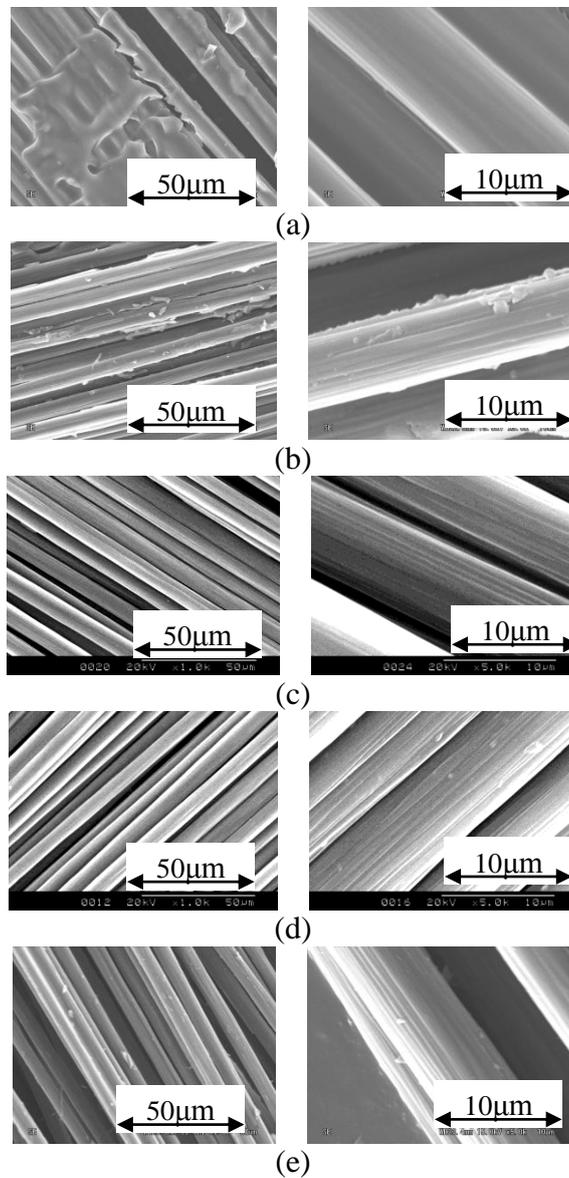
2.4.2 Results and discussion

2.4.2.1 CFRP pyrolysis by superheated steam

Pyrolysis was carried out at different times at 340°C, and different temperatures for 30 min. In the pyrolysis process, the CFRP were heated in the absence of oxygen. Under these conditions (Table 2-4), resin breaks down into lower molecular weight organic substances (gases); there was also a solid carbon char product. The recycled fibers were orderly and had the potential to be used as a feedstock for further CFRP re-manufacture, which can fully exploit the excellent mechanical properties of fibers for enhance the value of recycling.

2.4.2.2 Surface morphology

The reclaimed carbon fibers were analyzed by SEM. All the SEM micrographs of the reclaimed carbon fibers in Fig.4 were from CFRP (left column, reclaimed fibers at 1000× magnification; right column, close-up view of a single glass fiber at 5,000× magnification). In low magnification micrographs (1000×), we were able to observe the char that remained on carbon fibers; In high magnification micrographs (5000×), we were able to scrutinize the damage of carbon fibers.



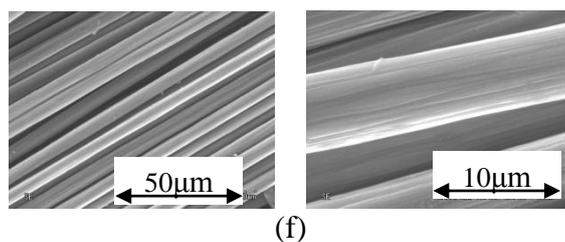


Fig. 2-16 SEM micrographs of recycled CFs from pyrolysis of CFRPs under different decomposition conditions: (a) reclaimed at 340°C for 15min, (b) reclaimed at 340°C for 30min, (c) reclaimed at 390°C for 30min, (d) reclaimed at 440°C for 30min, (e) reclaimed at 340°C for 60min, (f) reclaimed 340°C for 90min

The pictures presented in Fig. 2-16 (a) were SEM micrographs of recycled carbon fibers, which were reclaimed under the condition of 340°C for 15 minutes. Likewise, those of Fig. 2-16 (b) were reclaimed under the condition of 340°C for 30 minutes. Those of Fig. 2-16 (c) were reclaimed under the condition of 390°C for 30 minutes. Those of Fig. 2-16 (d) were reclaimed under the condition of 440°C for 30 minutes. Those of Fig. 2-16 (e) were reclaimed under the condition of 340°C for 60 minutes. Those of Fig. 2-16 (f) were reclaimed under the condition of 340°C for 90 minutes.

In the low magnification micrographs of Fig. 2-16 (a), Fig. 2-16 (b), more char impurities remained on the fiber's surface after the superheated steam treatment than on virgin fibers (Fig.2-17). In the low magnification micrographs of Fig. 2-16 (c), Fig. 2-16 (d), Fig. 2-16 (e), Fig. 2-16 (f), the fiber's surface is almost char-free. Under conditions of the same pyrolysis times and different pyrolysis temperature (low magnification micrographs of Fig. 2-16 (b), Fig. 2-16 (c) and Fig. 2-16 (d)), there are more char impurities could be observed in Fig. 2-16 (b), however, the fiber's surface is almost char-free in Fig. 2-16 (c) and Fig. 2-16 (d). It indicated that char impurities would decrease with a rise of temperature. Under conditions of the same pyrolysis temperature and different pyrolysis times (low magnification micrographs of Fig. 2-16 (a), Fig. 2-16

(b), Fig. 2-16 (e) and Fig. 2-16 (f)), there were more char impurities remained on fibers in the micrographs of Fig. 2-16 (a) and Fig. 2-16 (b) than that of Fig. 2-16 (e) and Fig. 2-16 (f). It could be considered that char impurities were reduced with the increase in pyrolysis time. To sum up the above mentioned, temperature and time may be crucial parameters which influence on pyrolysis. In addition, no physical damage (e.g., fissures or cracks) or morphological changes (e.g., in diameter or surface roughness) were observed in all SEM micrographs of 5000 \times .

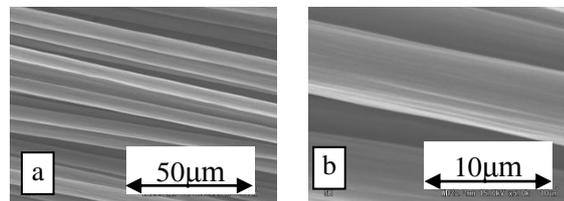


Fig.2-17 SEM micrographs of virgin carbon fiber at (a) 1000 \times , (b) 5000 \times magnification

2.4.2.3 Virgin carbon fibers heated under different atmospheres

The curve of tensile strength vs heating temperature of heated virgin carbon fibers was plotted in Fig. 2-18. Horizontal axis is heating temperature, and ordinate axis is tensile strength of carbon fibers. Horizontal line is tensile strength of unheated carbon fibers. Blue line is the tensile strength of carbon fibers heated under superheated steam atmosphere, and red is heated under inert atmosphere, black is heated under air atmosphere. Tensile strength of carbon fibers degenerated beginning at 300 $^{\circ}$ C. There was nearly the same variation between three kinds of carbon fibers which heated under different atmosphere. Only about 5% decrease is showed at 400 $^{\circ}$ C. Superheated steam atmosphere could be considered as three kinds of parameters: steam (H₂O), absence of

oxygen and high temperature. Inert atmosphere could be considered as two kinds of parameters: absence of oxygen and high temperature. Air atmosphere could be considered as two kinds of parameters: oxygen and high temperature. From the results of superheated steam atmosphere and inert atmosphere, we can infer that steam is not a crucial parameter which influence on tensile strengths. Tensile strength of carbon fiber doesn't drop until 1500 °C in inert atmosphere, but dropped begin at 400°C in air atmosphere. It could be considered that there is small quantity of oxygen in the superheated steam atmosphere, which dissolved in water tensile, and inert atmosphere, which is impure and contained small quantity of oxygen.

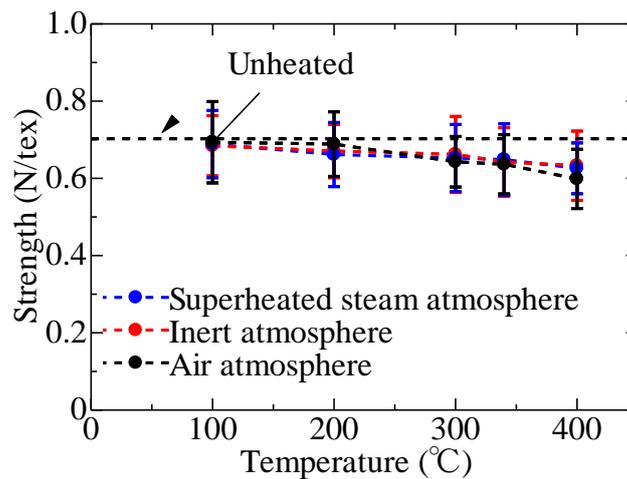


Fig.2-18 The variation in tensile strength of virgin carbon fibers with increasing temperature under different atmosphere

2.4.2.4 Mechanical properties of recycled carbon fibers

Studying on the mechanical behavior of recycled carbon fibers is valuable to validate the recycling processes and to identify major weaknesses in the recyclates. It's essential to investigate mechanical property in-depth. Understanding the relationships between pyrolysis conditions, mechanical properties and pyrolysis mechanisms of CFRP

provides information to analyze optimal pyrolysis point.

Figure 2-19 plotted the tensile strength vs pyrolysis temperature curve of recycled carbon fibers, which were reclaimed from decomposing CFRP under a constant time (30 min). The horizontal axis represented pyrolysis temperature, and the vertical axis represented tensile strength. Horizontal line is tensile strength of untreated virgin carbon fibers. The strength of recycled carbon fibers is lower than that of the virgin fiber at the temperature of 390°C and 440°C. However the strength of recycled carbon fibers is a little higher than that of virgin carbon fibers at the temperature of 340°C. It could be considered as that an incomplete decomposition occurred at 340°C. Resin cannot be pyrolyzed completely when the temperature is lower than 340°C, and fiber bundles (held together by minimal amounts of residual resin not completely pyrolyzed) increase the tensile strength of the recycled carbon fibers.

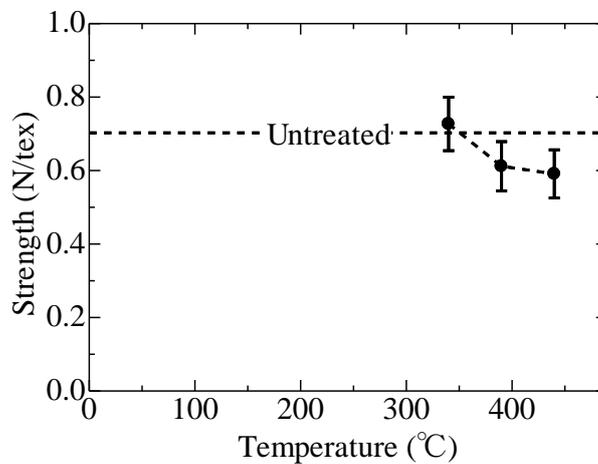


Fig.2-19 Tensile strength vs pyrolysis temperature curve of recycled carbon fibers reclaimed by pyrolyzing CFRP for 30 min

Figure 2-20 plotted the tensile strength vs pyrolysis time curve of recycled carbon fibers, which were reclaimed from CFRP under a constant temperature (340°C). The horizontal axis represented pyrolysis time, and the vertical axis represented tensile

strength. Horizontal line is tensile strength of untreated virgin carbon fibers. The tensile strength of recycled carbon fibers is reduced with the increase in pyrolysis time. Under the condition of pyrolysis time of 30 min and pyrolysis temperature of 340°C, the tensile strength of recycled carbon fibers is a little higher than that of virgin carbon fibers. The tensile strength of recycled carbon fibers is obviously higher than that of virgin carbon fibers for 15 min, and is lower than that of virgin carbon fibers for 60 min and 90 min.

It also can be considered as that an incomplete decomposition occurred for 15 min and 30 min. Resin cannot be pyrolyzed completely, and fiber bundles increase the tensile strength of the recycled carbon fibers.

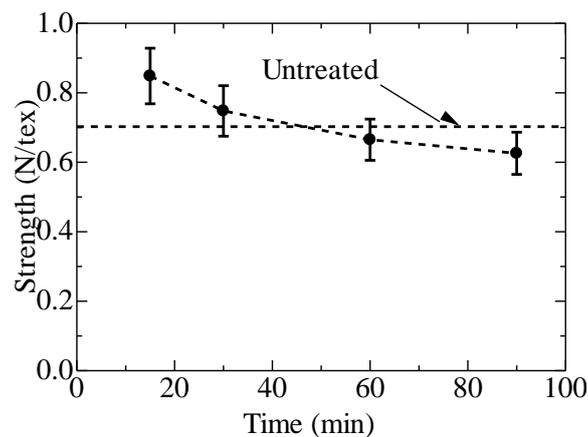


Fig.2-20 Tensile strength vs pyrolysis time curve of recycled carbon fibers reclaimed by pyrolyzing CFRP at 340°C

In order to reuse the recycled carbon fibers for remanufacturing CFRP, the value of tensile strength of recycled carbon fibers is a yardstick to evaluate the conditions under which the CFRP were decomposed. Pyrolysis under the conditions of 340°C for 30 min and 340°C for 15 min, the tensile strength of recycled fiber is higher than that of virgin fiber. In consideration of interfacial adhesion between recycled carbon fibers and new

resin when remanufacturing CFRP, residual resin (or char impurities) should be reduced as much as possible. Of course, it should be set high tensile strength as a prerequisite. Therefore, condition of 340°C for 30 min, comparatively, is optimal condition CFRP in this study.

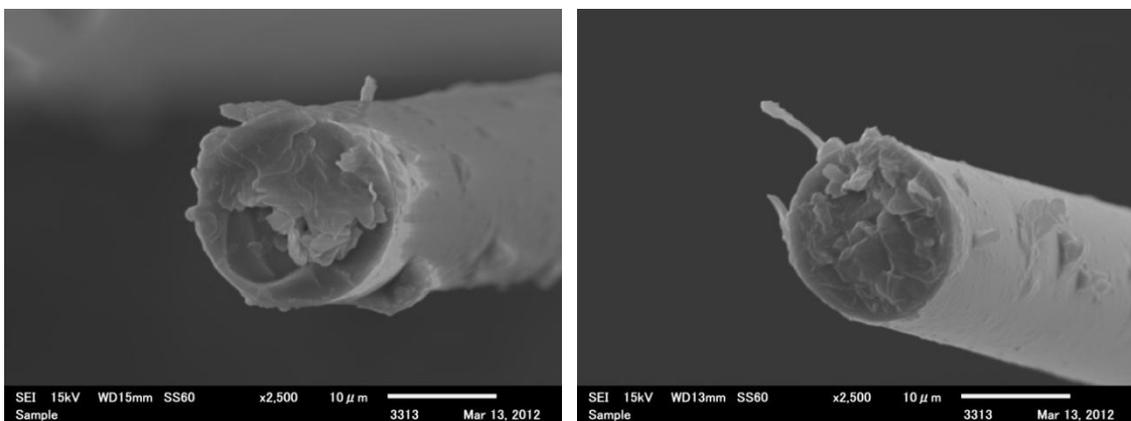
Figure 2-18 (blue line) shows the variation of tensile strength that carbon fibers (only) heated under superheated steam atmosphere. Figure 2-19 and Figure 2-20 show variation of tensile strength that carbon fibers which recycled from pyrolyzing CFRP under superheated steam atmosphere. When the tensile strength of recycled carbon fibers is lower than virgin carbon fibers, it can be considered as that resin is pyrolyzed completely, and carbon fibers are exposed to superheated steam atmosphere. It can be assumed to be the equal to a condition of carbon fibers (only) heated under superheated steam atmosphere. From above, it can be considered that there are two steps in the pyrolysis process. The first step: resin is pyrolyzed into lower-weight molecules until a coming of complete pyrolysis. The second step: carbon fibers are exposed to superheated steam atmosphere. Refer to the results of Figure 2-18, it gives a summation that until resin completely pyrolyzed, carbon fibers are protected and prevented the temperature from affecting the tensile strength of carbon fibers. In order to obtain high value recycled carbon fibers, when resin is about to completely pyrolyzed, carbon fibers should be took out of superheated steam atmosphere as soon as possible. Even though a litter resin remained on the surface of carbon fibers, interfacial adhesion would improve by surface treatment in future.

2.5 Mechanism of pyrolysis of fiber reinforced plastic

From above, we can see fiber strength loss after recycling, except those recycling

under optimal pyrolysis conditions. Fracture surfaces of fibers before and after heat treatment were examined using scanning electron microscopy to identify the failure mechanism. Scanning electron images representative of the fracture surfaces of unheated glass fibers are presented in Fig. 2-21. It should be noted that the fractured surfaces of unheated glass fibers show a rough surface. A large smooth region is observed in Fig. 2-22, which exposed to superheated steam atmosphere, and heated for 370 °C and 30 min.

During manufacture, an open glass pore structure is frozen-in under rapid cooling as validated by the increasing density of glass fibers and compaction during annealing [41]. So there are many micro-cracks on the surface of the virgin glass fiber. Crack growth occurred when glass fiber exposed to high temperature atmosphere. It is strongly supported by Fig. 2-21 and Fig. 2-22.



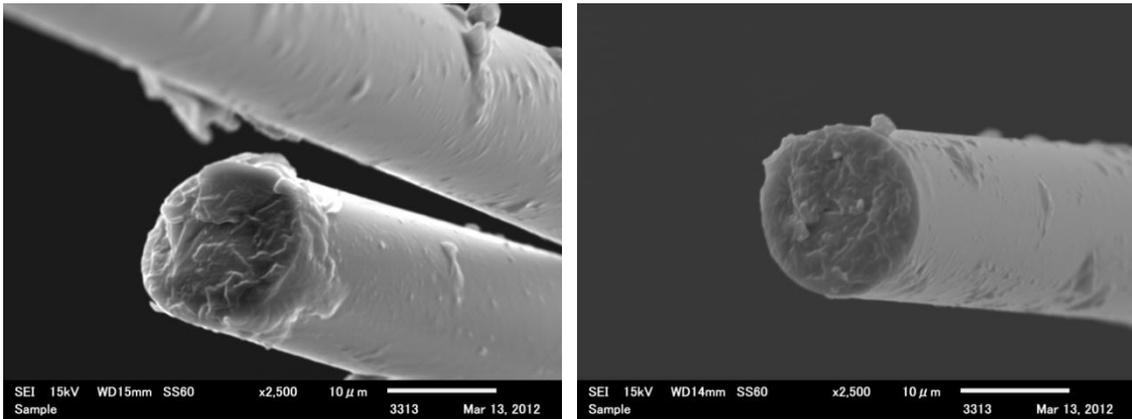


Fig. 2-21 SEM micrographs of the tensile fractured surfaces showing the transverse cross-section morphology of unheated glass fiber

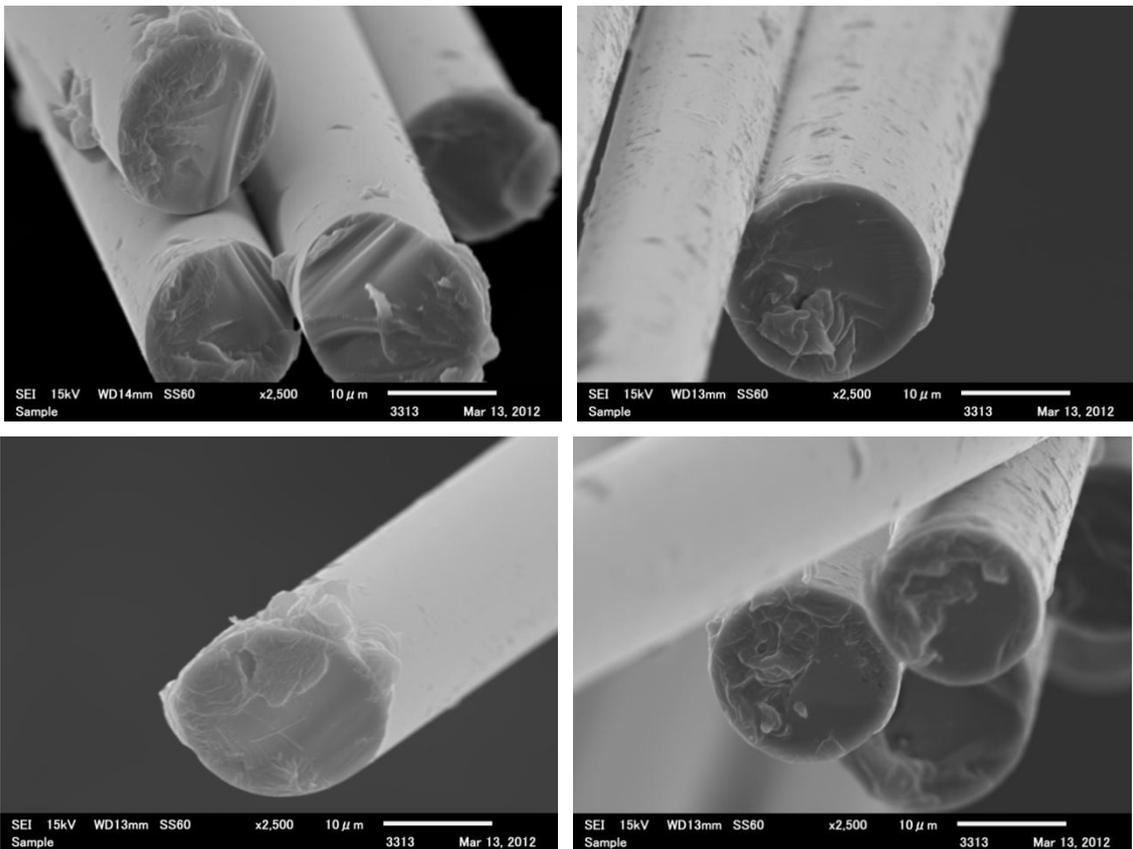


Fig. 2-22 SEM micrographs of the tensile fractured surfaces showing the transverse cross-section morphology of heated glass fiber

A similar result could be obtained for carbon fiber from Fig. 2-23 and Fig. 2-24. The fractured surfaces of unheated carbon fibers show a rough morphology, with no smooth region as shown in Fig. 2-23. A smooth region is observed in Fig. 2-24, which exposed to superheated steam atmosphere, and heated for 400 °C and 30 min. It could be attributed to the defect of carbon fiber which created during manufacture and oxidized by extremely small quantity of oxygen when heating process. These lead to crack growth and result a loss of strength.

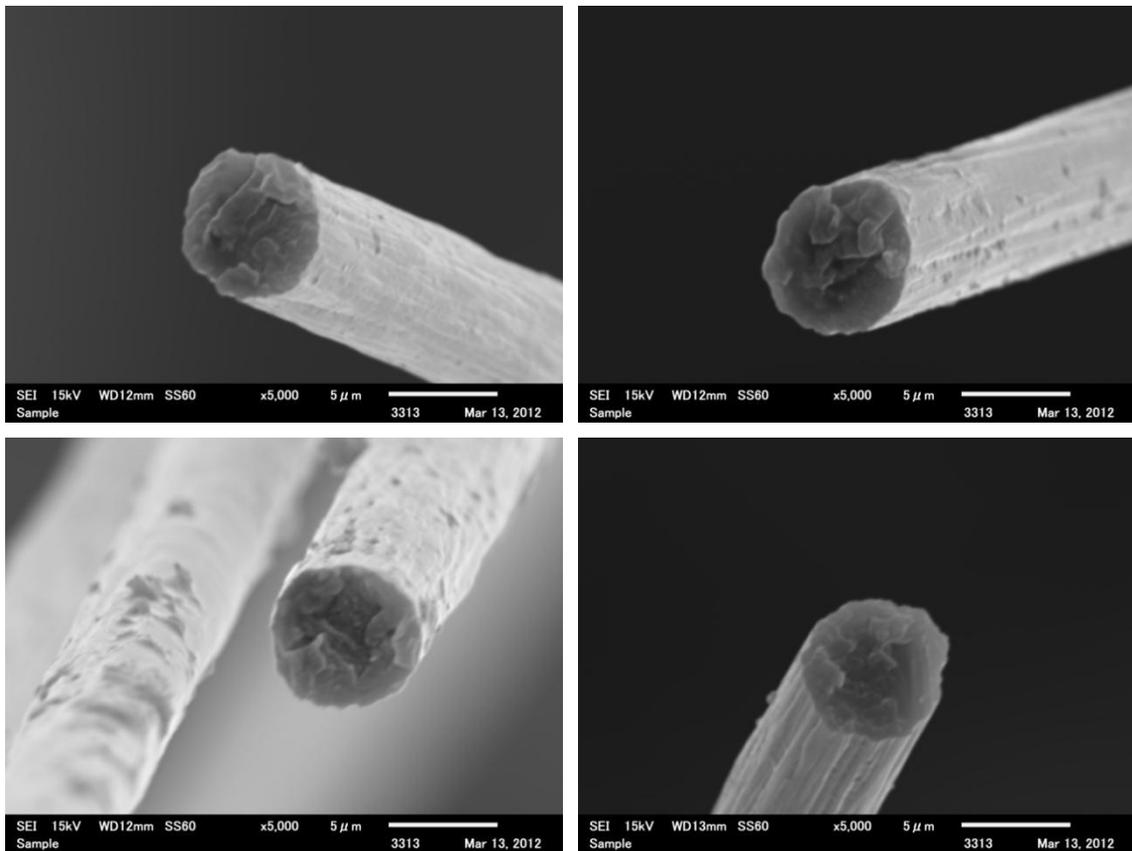


Fig. 2-23 SEM micrographs of the tensile fractured surfaces showing the transverse cross-section morphology of unheated carbon fiber

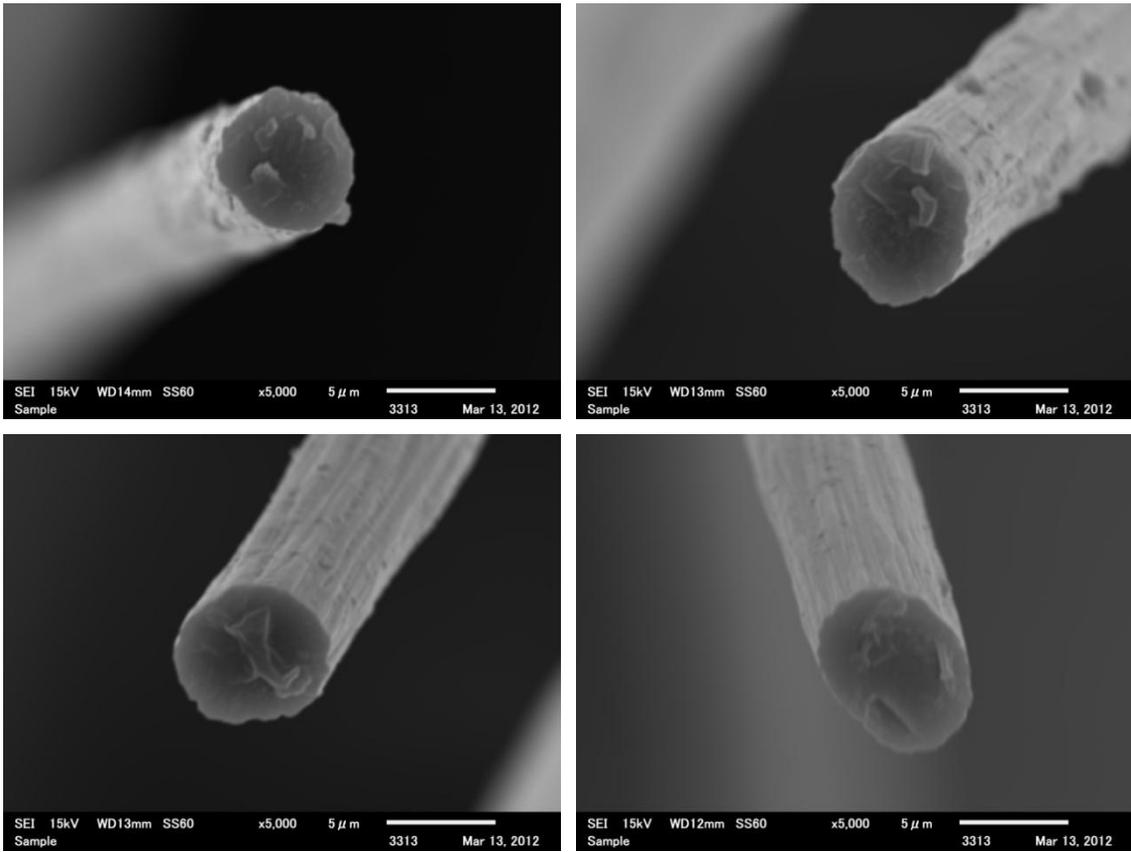


Fig. 2-24 SEM micrographs of the tensile fractured surfaces showing the transverse cross-section morphology of heated carbon fiber

From above mentioned, once fiber exposed to heating atmosphere (which maybe contains small quantity of oxygen), fiber strength loss will occur. However, the strength of fiber which recycled under optimal pyrolysis conditions didn't reduce. It could be attributed to the resin which wrapped up the fiber that protected from high temperature and small quantity of oxygen. The fibers were completely cut off from environment by resin to avoid strength loss. The reason why strength of fiber recycled under optimal pyrolysis conditions didn't reduce could be explained as Fig. 2-25. The strength of fibers didn't reduce before resin pyrolysis as step1 depicted in Fig. 2-25. Fibers began to lose strength during thermal recycling when the resin reduced to amount of just wrap

up the fiber as step2. The strength of fibers dropped once the amount of resin reduced than step2, the fibers exposed to heating atmosphere, as step3 depicted in Fig. 2-25. The strength of fibers dropped slowly and became constant finally, which was depicted as step4.

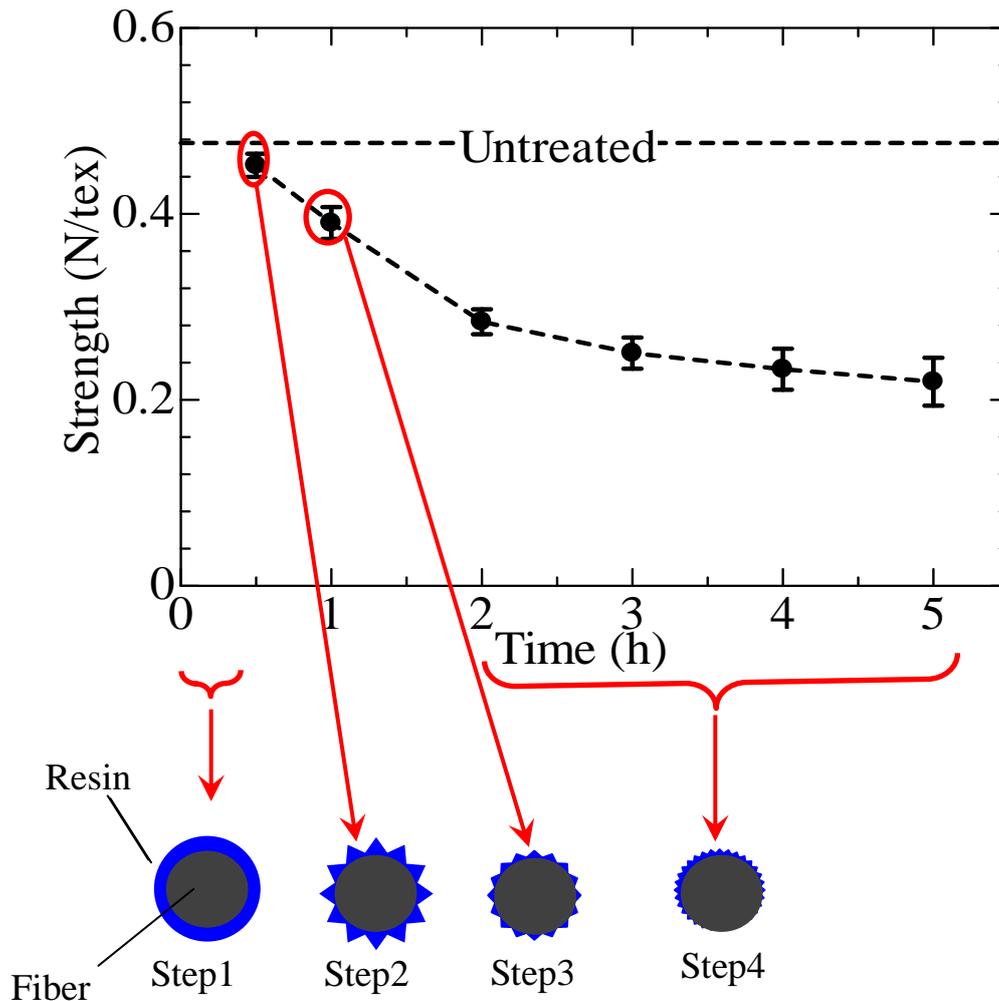


Fig. 2-25 Mechanism of pyrolysis of fiber reinforced plastic

2.6 Summary

In chapter 2, the recycling of GFRP by pyrolysis was investigated in superheated steam for times ranging from 30 to 300 min at 340, 370, and 450°C. The recycling of CFRPs by pyrolysis was investigated in superheated steam for times ranging from 15 to 90min at 340°C, 390°C, and 440°C. Experiments performed in superheated steam

provided resin removal efficiencies above 80wt%. Some char residue from the polymer remaining on the fibers may limit reuse options or require further processing for removal. The results of virgin fibers heated in different atmospheres indicate that high temperature and small quantity of oxygen are the main factors affecting the tensile strength of recycled fibers. Therefore, setting the temperature of pyrolysis as low as possible to obtain high-value recycled fibers is significant. Glass fibers of good mechanical quality were recovered from GFRP by using superheated steam. The tensile strength of the fibers was 3 to 5% lower than that of the virgin fibers under the optimal condition. The tensile strength of carbon fibers is near that of virgin fibers under optimal conditions, and this result is promising. The optimal pyrolysis conditions for GFRP and CFRP were determined. In this research, the optimal condition of GFRP was 370 °C and 30min, the optimal condition of CFRP was 340 °C and 30min. Under optimal condition, strength of recycled fiber dropped slightly. The reason why strength of fiber recycled under optimal pyrolysis conditions didn't reduce could be attributed to the resin which wrapped up the fiber that protected from high temperature and small quantity of oxygen.

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CHAPTER THREE

Recycling and reusing of plastic

Chapter3 Recycling and reusing of plastic

3.1 Introduction

From chapter2, we know that studies on recycling of fiber reinforced resin composites could be classified into three types[1]: mechanical recycling [2-4], thermal processes [5-12] and chemical recycling [13-31]. Each technology could recycle fiber and plastic from recycling process.

In mechanical recycling process, it is difficult to separate recycled materials into fiber and plastic. It would be segregated by sieving into powdered products (rich in resin) and fibrous products (rich in fibers) [4,32-34]. The powdered products (rich in resin) are usually reused as fuel or filler of concrete and cement composites[33-34].

In thermal processes, plastic is volatilized into lower-weight molecules organic substances. It is difficult to reuse as resin by re-polymerization. So it is usually reused as fuel[5-12].

Chemical recycling process can be used to decompose the plastic into its original monomers. It is most desirable to transform waste plastic into potential feedstock through chemical recycling. Chemical recycling is not effective to recycle the composites because not all the solution is feasible to all composites. Chemical process is very costly, for both expensive equipment and chemical agent. One other problem is recycling of chemical agent[1].

In this research, the recycling method is one kind of pyrolysis. Plastic is volatilized into lower-weight molecules organic substances in in a pyrolysis process. It is difficult to reuse as resin by re-polymerization. So we propose that it can be reused as fuel. We developed a plastic recycling subsystem device to recycle pyrolysis oil. The calorific

value of recycled pyrolysis oil was measured by bomb calorimeter. To evaluate whether recycled pyrolysis oil can be used as fuel.

3.2 Development of plastic recycling subsystem

Top priority was given to the check of decomposed materials. The aim of plastic recycling subsystem is simple and could cool down to room temperature. From the past research, it could forecast that heavy oil and gas could be collected after condensation of gas stream. So a method of diving high temperature gas stream, mixture of steam and low weight molecules organic gas, into cool water. It is easy to condense low weight molecules organic gas and recycle pyrolysis oil.

Plastic recycling subsystem is devised two tank structures in this research. The mixed gas contains low weight molecules organic will be cooled and condense in the first tank, which is vacant and immersed into cool water. Surplus gas, which cannot cool in the first tank, will be guided into the second tank which filled up with cool water. Small amount of surplus gas will cool and condense. Moreover, it is designed the first tank plays the role of the water trap, even if the pipe soaks the water of the second tank, regurgitation will never cause in the recycling process. Fig. 3-1(a) shows the schematic view of the plastic recycling subsystem device. Fig. 3-1(b) shows three dimensional CAD drawing of the first tank and the structure inside. Part (1) joined the superheated steam decomposition equipment exhaust pipe and plastic recycling subsystem together. The mixed gas flows into the first tank through part (1). In order to extend cool time, the period of mixed gas stay in the first tank is extended by attaching the division plate which marked (2) in the Fig. 3-1(a). Surplus gas, which cannot cool in the first tank, will be guided into the second tank through the metallic flexible hose, which marked (3)

in the Fig. 3-1(a). The second tank is filled up with cool water. Surplus gas passes through (3), submerges in water to condense into pyrolysis oil.

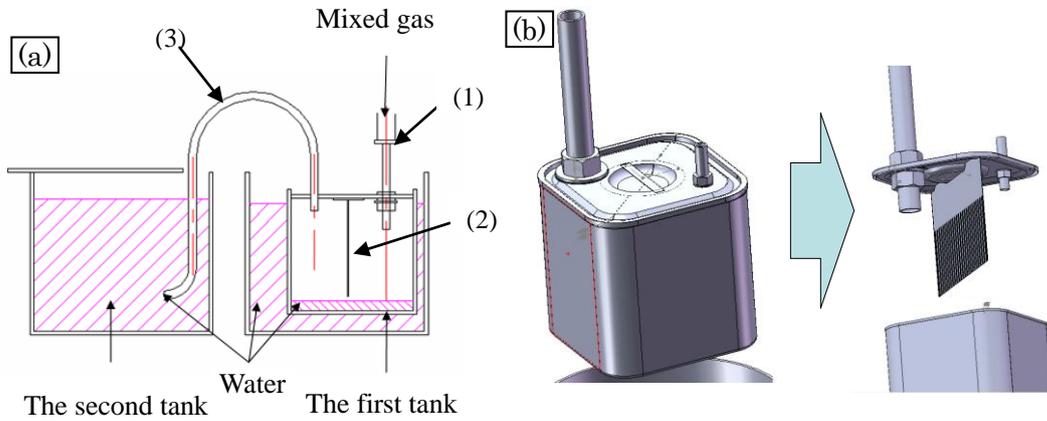


Fig. 3-1 Schematic view of the plastic recycling subsystem device. (b) Three dimensional CAD drawing of the first tank and the structure inside

3.3 Plastic recycling experiment

3.3.1 Materials

GFRP and CFRP were employed to carry on the plastic recycling experiment. GFRP was manufactured using unidirectional glass fibers, purchased from Unitika Ltd., and unsaturated polyester resin, obtained from Showa Highpolymer Co., Ltd by vacuum-assisted resin transfer molding (VARTM). CFRP was manufactured using PAN-based T300 woven carbon fiber, produced from Toray Industries Inc. and epoxy resin, obtained from Nagase ChemteX Corporation by VARTM.

3.3.2 Pyrolysis experiment

Sample were put into chamber and pyrolyzed under the optimum decomposition conditions which summarized from chapter2. The pyrolysis conditions were listed in

Table3-1.

Table 3-1. Pyrolysis conditions

Sample	Pyrolysis temperature (°C)	Pyrolysis time (min)
GFRP	370	30
CFRP	340	30

3.3.3 Fourier transforms infrared (FTIR) spectroscopy

FTIR spectra of different modified starches were recorded on a Fourier transform infrared spectrometer (IRPrestige-21, Shimadzu Co., Ltd., Japan) in a range of wave numbers from 4000 to 400 cm⁻¹.

3.3.4 Calorific values and energy production

The calorific value (kJ g⁻¹) of the recycled pyrolysis oil was determined according to JIS M8814 (Japanese Industrial Standards Committee) with an automated bomb calorimeter (CA-4AJ, Shimadzu Co., Ltd., Japan).

3.4 Results and discussion

3.4.1 Pyrolysis experiment

Pyrolysis oil was sticking to inner wall of the first tank of plastic recycling subsystem device. It also precipitated in water at the bottom of the first tank. The amount of pyrolysis oil at the bottom of the first tank was more than that sticking to inner wall. Pyrolysis oil was able to collect using spatula. The collected pyrolysis oil showed in Fig. 3-2. Moreover, in the second tank, the amount of pyrolysis oil mixed with steam was

low. The pyrolysis oil was cooled and float on water. It was difficult to collect pyrolysis oil like that in the first tank. It only can be collected with water. It also showed that plastic recycling subsystem successful recycled plastic by above mentioned structure, and the first tank played an important role to cool mixed steam to condense into pyrolysis oil.

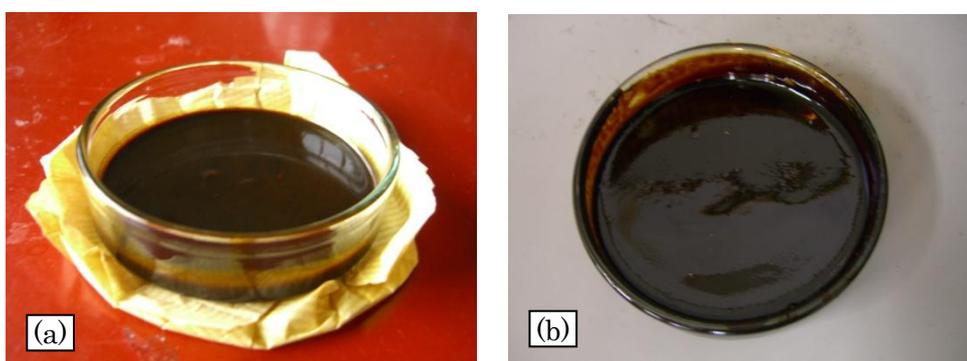


Fig. 3-2 The collected pyrolysis oil. (a) recycled unsaturated polyester resin; (b) recycled epoxy resin.

3.4.2 FTIR spectroscopy

As mentioned above, the unsaturated polyester resin was heated at 370 °C for 30 min and then analyzed by Fourier Transform Infrared (FT-IR). The FT-IR spectra of them showed in Fig. 3-3.

The unsaturated polyester resin showed important characteristic absorption bands at 1732 cm^{-1} for carbonyl group (C=O), 2800-3060 cm^{-1} for acid functional group (COOH) and 1629 cm^{-1} for aromatic C=C stretching[35]. The peaks at 1166 cm^{-1} and 1263 cm^{-1} band appeared for C–O–C stretching vibrations attached with aliphatic and aromatic moiety. The interpretation of the spectra obtained was made by comparison with the spectrum of the raw resin. From the FTIR spectrum of recycled unsaturated

polyester resin, it was seen that the absorption peaks were almost similar to raw unsaturated polyester resin. The spectrum related to the resin heated at 370 °C showed an increase in the intensity of the acid functional group vibration bands at 2800-3060 cm^{-1} . We observed a reduction of the intensity of the (-C-O-C-) stretching vibration band of the ester functional group at 1150-1380 cm^{-1} . These results confirm the degradation of the unsaturated polyester resin and were in line with the pyrolysis recycling process given by section 3.1.

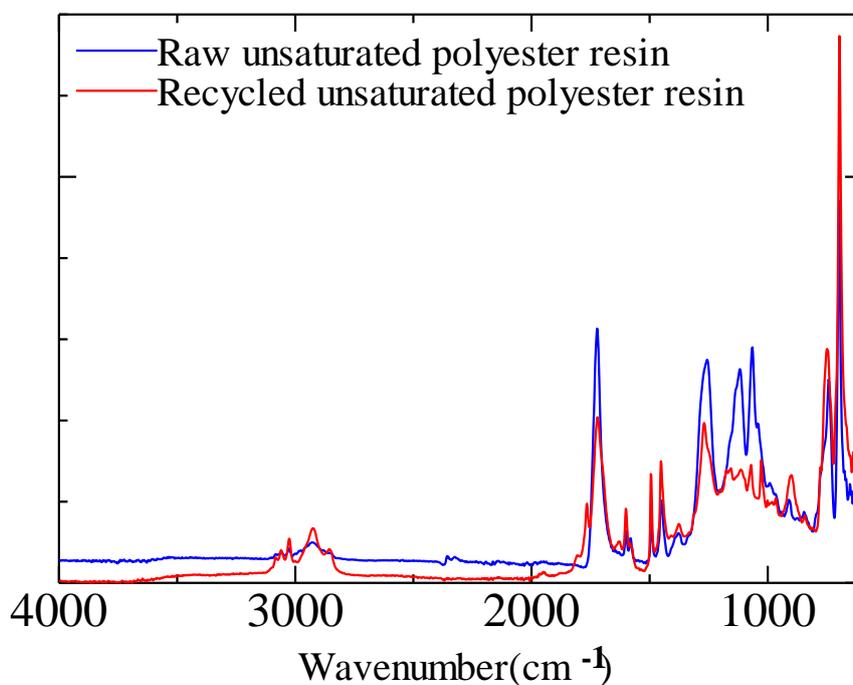


Fig. 3-3 FT-IR spectra of the raw unsaturated polyester resin and that recycled at 370 °C

The epoxy resin was heated at 340 °C for 30 min and then analyzed by Fourier Transform Infrared (FT-IR). The FT-IR spectra of them showed in Fig. 3-4. In Fig. 3-4, the characteristic peaks of the materials were depicted, including those at 1609 cm^{-1} (C-C skeletal stretching), 1036 cm^{-1} (aromatic deformation), and 915 cm^{-1} (epoxide

ring)[36]. From the FTIR spectrum of recycled epoxy resin, it was seen that the absorption peaks were almost similar to raw epoxy resin. A reduction of the intensity of aromatic deformation at 1036 cm^{-1} was observed. It revealed that degradation occurred during pyrolysis recycling process.

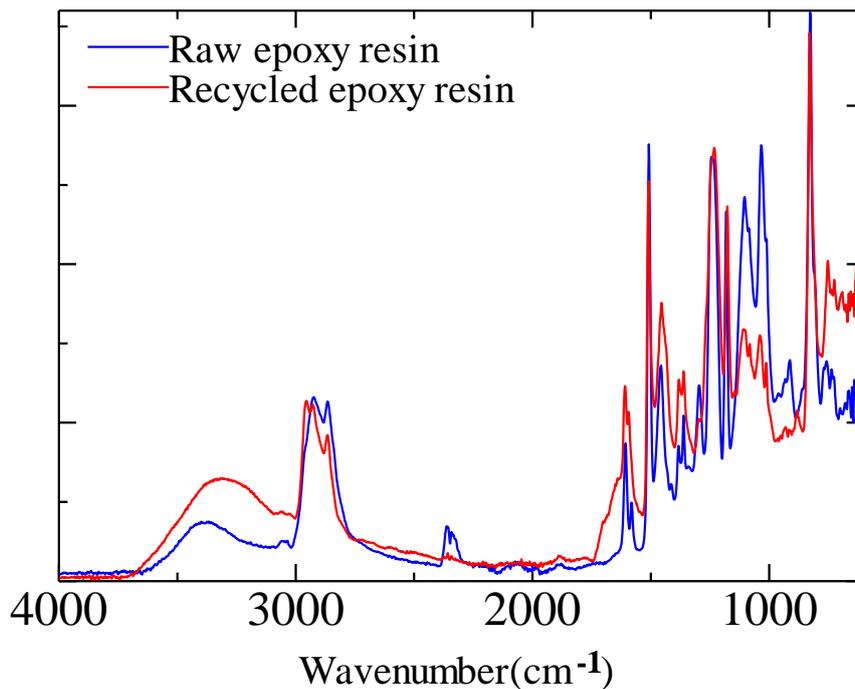


Fig. 3-4 FT-IR spectra of the raw epoxy resin and that recycled at 340 °C

3.4.3 Fuel quality

The bomb calorimeter was the most common device for measuring the heat of combustion or calorific value of a material. The calorific values of recycled pyrolysis oil and other conventional fuel were listed in Table 3-2. Calorific value of recycled pyrolysis oil was a little lower than that of diesel, petrol and kerosene, higher than wood (15% water), the same as steam coal (1% water). It was possible to use recycled pyrolysis oil as a fuel in the further.

Table 3-2. Calorific values of recycled pyrolysis oil and other conventional fuel[6].

Fuel	kJ g⁻¹
Recycled pyrolysis oil	36.3
Diesel	46.0
Petrol	44.8-46.9
Kerosine	47.0
Steam coal (1% water)	36.0
Wood(15% water)	16.0

3.5 Summary

In chapter3, it is possible to recycle plastic using designed plastic recycling subsystem device. From the results of FT-IR, it is confirm that plastic degraded during pyrolysis recycling process. From the results of calorific values and energy production, it is confirm that recycled pyrolysis oil could be used as a fuel in the further.

The reduction of the intensity of the (-C-O-C-) stretching vibration band of the ester functional group and aromatic deformation revealed that degradation occurred. Molecular weight of recycled pyrolysis oil is lower than raw of them.

It turned out that recycled pyrolysis epoxy oil contained about 30.2 kJ g⁻¹ calories and recycled pyrolysis unsaturated polyester oil contained about 36.3 kJ g⁻¹. While heavy oil contained about 40 kJ g⁻¹ calories. It is possible to use recycled pyrolysis oil as a fuel.

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CHAPTER FOUR

Surface cleaning of recycled fibers and static mechanical property of recycled fiber reinforced plastic composites

Chapter 4 Surface cleaning of recycled fibers and static mechanical property of recycled fiber reinforced plastic composites

4.1 Introduction

The use of FRP composites as high-performance materials is increasing in the aerospace, military, automobile, and sports industries. However, FRP is one of the most difficult materials to separate into elemental components (e.g., fiber, filler, and polymers). As a result, for many years FRP materials have been incinerated or used for landfill without any recyclings[1-2]. Although researchers have developed new technologies[3-32] to recycle FRP, fibers obtained through these technologies are either short or fluffy, and they are not treated after recycling by those technologies. Orderly longer recycled fibers are more valuable. Thus, we developed a new recycling technology using a steam system. Our previous studies[33-34] indicated that recycling FRP by superheated steam is optimal, making it possible to obtain long fibers with little decline in tensile strength.

The performance of FRP depends on fiber and resin characteristics. In particular, the interfacial adhesion between fibers and resin plays an important role in improving the mechanical behavior of FRP. Good interfacial adhesion between fiber and resin is necessary to ensure effective load transfer from one fiber to another through the resin. Generally, the methods of enhancing interfacial bonding strength can be classified into two fundamental categories: modifying the fibers and applying a toughened resin[35-37]. The interfacial characteristics between fiber and resin depend mainly on

the fiber surface.

High-value recycled reinforced fiber with high performance can be remanufactured into FRP for reuse. In this study, the resin impurities that remained on the fibers would affect the performance of recycled fiber reinforced polymer (R-FRP). Therefore, it was necessary to treat the surface of recycled fibers to enhance the interfacial bond between fibers and resin in a composite. We removed the residual resin impurities by soaking the recycled fiber in solution. Treated recycled glass fibers (TR-GFs) and recycled carbon fibers (TR-CFs) were remanufactured by vacuum-assisted resin transfer molding (VARTM), and the bending properties of the R-FRP composites were determined and compared.

4.2 Materials and methods

4.2.1 Manufacturing of virgin fiber-reinforced polymer (V-FRP)

Commercially available unidirectional glass fibers, purchased from Unitika Ltd., were used as the reinforcement fiber of GFRP. Unsaturated polyester resin, obtained from Showa Highpolymer Co., Ltd., was used as the matrix in the present work. Pamekku N was chosen as the hardener and was purchased from Nof Corporation. Unsaturated polyester resin and hardener were 100 and 0.8 parts by weight. PAN-based T300 carbon-fiber fabrics used in the present study were produced by Toray Industries Inc. Epoxy resin obtained from Nagase ChemteX Corporation was used as the matrix of carbon fiber reinforced polymer (CFRP). Hardener was also purchased from Nagase ChemteX Corporation. Epoxy resin and hardener were 100 and 27 parts by weight. These materials are listed in Table 4-1. The prepregs were fabricated by VARTM, cut into scrap ($50 \times 200\text{mm}^2$), and recycled by superheated steam.

Table 4-1 Materials for specimens

Type	Resin	Hardener	Fiber
GFRP	Unsaturated polyester resin (Showa High polymer, Japan)	Pamekku N (Nof, Japan)	Unidirectional glass fiber (Unitika, Japan)
CFRP	Epoxy resin XNR6815 (Nagase Chemtex, Japan)	XNH6815 (Nagase Chemtex, Japan)	Cloth carbon fiber fabrics (Toray, Japan)

4.2.2 Recycling of V-FRP

Samples were fed into the chamber of a superheated steam recycling instrument and heated in the absence of oxygen. GFRP samples were heated at 370°C for 30min [9]. CFRP samples were heated at 340°C for 30min [10]. After the experiment, samples were cooled to room temperature.

4.2.3 Treatment of recycled fibers

Recycled fibers were fixed by wire netting and soaked in solution to keep them in order. Recycled glass fibers (R-GFs) were soaked in acetone for 4h and in detergent for 24h at room temperature respectively. They were then cleaned by an ultrasonic washing machine for 1h. Recycled carbon fibers (R-CFs) were soaked in acetone for five days at room temperature and in N-Methyl-2-pyrrolidinone (NMP) for three days at 200°C respectively. They were then cleaned by an ultrasonic washing machine for 1h. These conditions are listed in Table 4-2. Treatment time mentioned in Table 4-2 was selected according to our preliminary testing experiments. TR-GFs and TR-CFs were

remanufactured by VARTM after drying. Figure 4-1 presents a schematic view of the experiment.

Table 4-2 Solutions for surface treatment

Recycled fibers	Surface treatment conditions		
	Solution	Temperature	Time
R-GFs	Acetone (Junsei Chemical, Japan)	Room temperature	4h
	Detergent (Kao, Japan)	Room temperature	24h
R-CFs	Acetone (Junsei Chemical, Japan)	Room temperature	5 days
	NMP (Kanto Chemical, Japan)	200°C	3 days

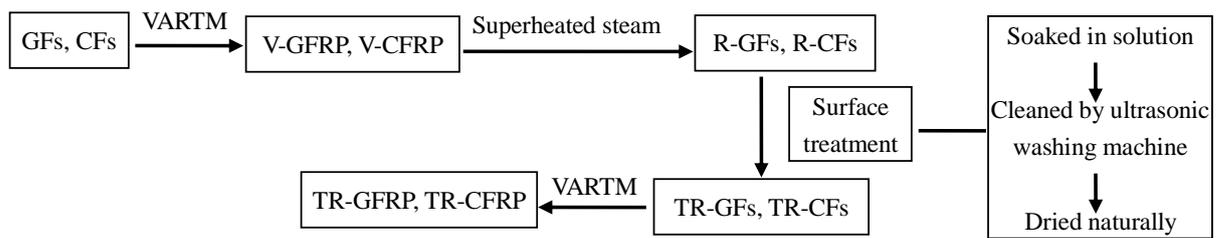


Fig. 4-1 Schematic view of the experiment.

4.2.4 SEM

Samples of R-GFs, R-CFs, virgin glass fibers (V-GFs), and virgin carbon fibers (V-CFs) were analyzed using scanning electron microscopy (SEM) (Hitachi S-3000N)

to determine the morphology and diameter of the fibers, as well as visual signs of residual resin impurities. The microscope was operated in high-vacuum mode, and images were obtained through a secondary electron detector.

4.2.5 Mechanical Testing

The mechanical properties of V-FRP, R-FRP, and TR-FRP composites were evaluated on an AUTO GRAPH (Shimadzu AG-20KND). The bending strength of the composites was measured by applying a three-point bending test according to the JIS K7017 standard procedure. The bending strength was taken as the average value of five tests.

4.3 Results and discussion

4.3.1 Recycling of V-GFRP and treatment of R-GFs

4.3.1.1 Surface morphology

The surface morphologies of R-GFs (Fig. 4-2 (a)) and V-GFs (Fig. 4-2 (b)) were examined by SEM at a magnification of 1000×. Considerable quantities of nubbles were clearly clinging to the surfaces of R-GFs (Fig. 4-2 (a)), whereas V-GFs exhibited a cleaner, smoother surface (Fig. 4-2 (b)). Unsaturated polyester resin impurities remaining on the fiber's surface would spoil the interfacial adhesion between fibers and new resin when they were remanufactured into recycled GFRP (R-GFRP). High-performance R-GFRP requires good interfacial adhesion. Therefore, surface treatment of R-GFs should be performed to improve interfacial adhesion between fibers and new resin.

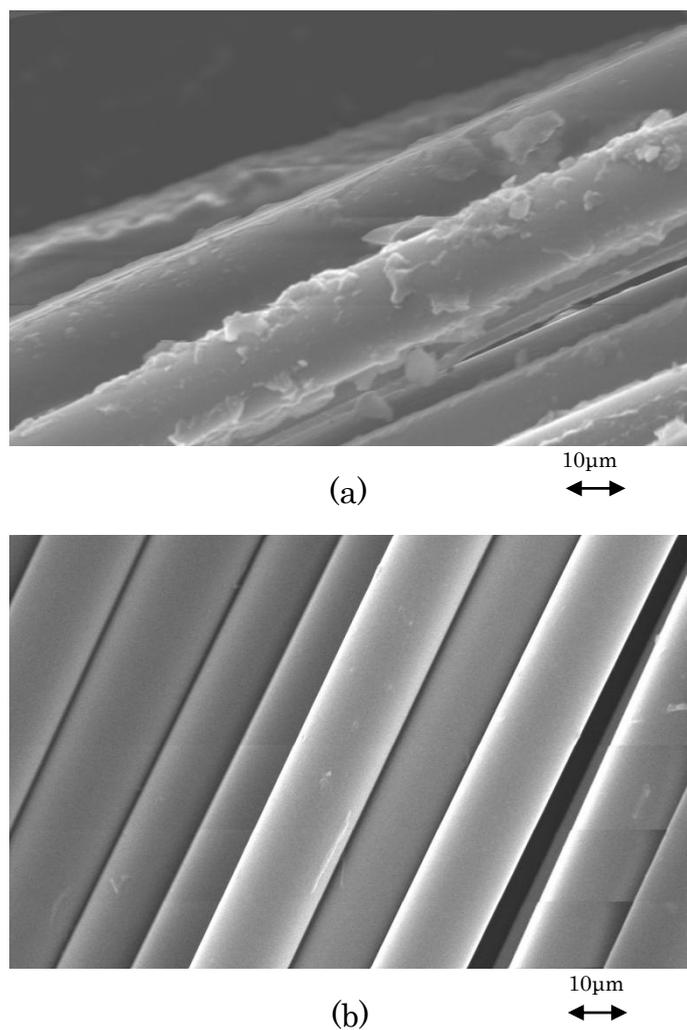


Fig. 4-2 SEM micrographs of fibers at 1000 \times magnification (a) R-GFs, (b) V-GFs.

Figure 4-3 (a) depicts the surface morphology of TR-GFs soaked in detergent for 24h and cleaned by an ultrasonic washing machine for 1h after soaking. Figure 4-3 (b) depicts that of TR-GFs soaked in acetone for 4h and cleaned by an ultrasonic washing machine for 1h after soaking. All were analyzed at a magnification of 1000 \times . The nubbles that could be observed clinging to the surfaces of TR-GFs were fewer and smaller than those depicted in Fig. 4-2 (a). Figure 4-3 (b) reveals a cleaner, smoother surface than Fig. 4-3 (a). It was nearly the same as that of V-GFs. The results indicated that both detergent and acetone effectively removed unsaturated polyester resin

impurities from the fiber's surface, although acetone was more effective than detergent. It was possible to improve interfacial adhesion between fibers and new resin when they were remanufactured into TR-GF reinforced polymer (TR-GFRP).

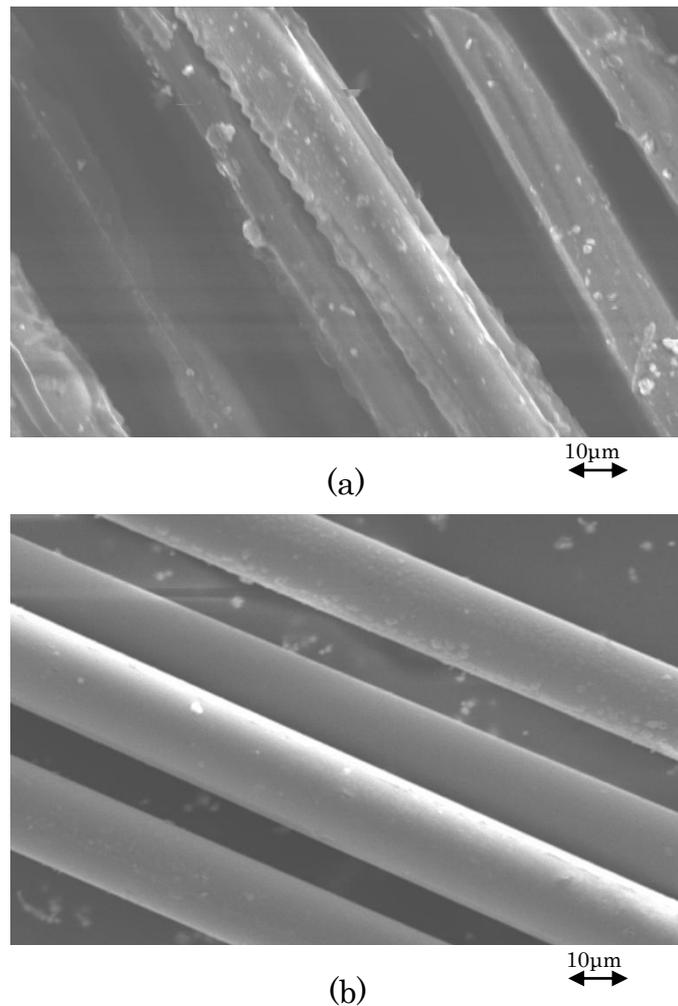


Fig. 4-3 SEM micrographs of TR-GFs at 1000× magnification (a) detergent, (b) acetone.

4.3.1.2 Mechanical properties

Detergent and especially acetone effectively removed the remaining unsaturated polyester resin impurities. However, whether the solutions would affect the fiber soaked

in them was not determined. Therefore, V-GFs were soaked in two different solutions and then fabricated to treated virgin glass fiber-reinforced polymer (TV-GFRP). The bending strength of TV-GFRP was measured and compared with that of V-GFRP.

Figure 4-4 compares the bending strengths of V-GFRP (circle), TV-GFRP reinforced by virgin glass fiber treated with detergent (triangle), and TV-GFRP reinforced by virgin glass fiber treated with acetone (square). The bending strengths of the three types were nearly the same. Thus, neither detergent nor acetone affected the bending strength of TV-GFRP. These solutions may be considered for unsaturated polyester resin impurity removal in the future.

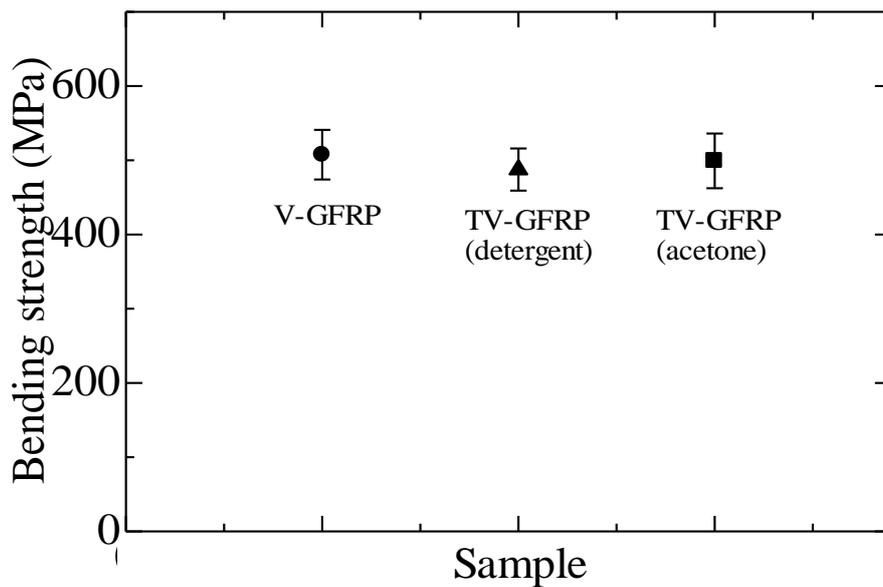


Fig. 4-4 Bending strength of V-GFRP and TV-GFRP (1) reinforced by V-GFs, (2) reinforced by V-GFs treated with detergent, and (3) reinforced by V-GFs treated with acetone

The results presented in section 4.3.1.1 indicate that both detergent and acetone

effectively removed unsaturated polyester resin impurities. Although the surface was cleaner than that of R-GFs, whether the bending strength would be improved by detergent and acetone, and how much it would be improved had not been determined. Thus, the bending strengths of V-GFRP, R-GFRP, and TR-GFRP were measured and plotted in Fig. 4-5.

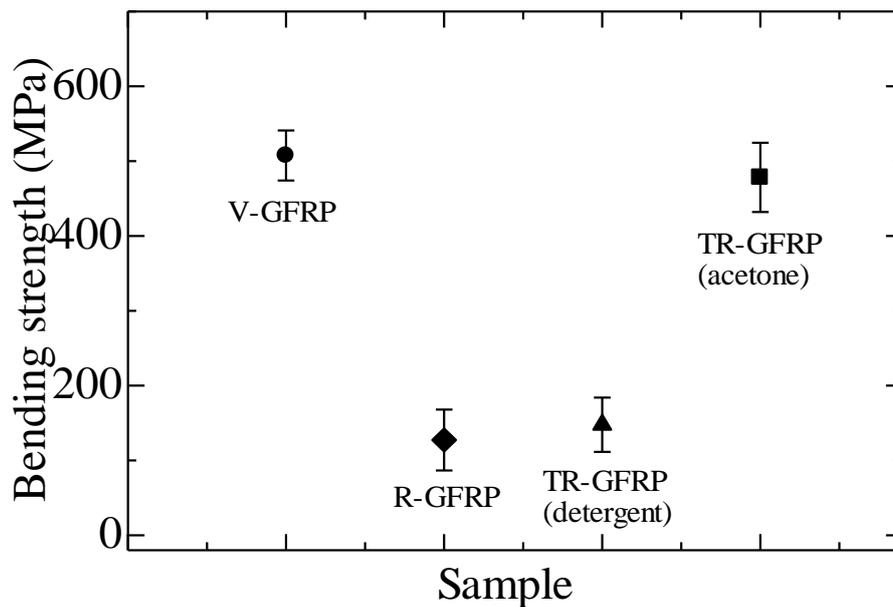


Fig. 4-5 Bending strengths of V-GFRP, R-GFRP and TR-GFRP (1) reinforced by V-GFs, (2) reinforced by R-GFs, (3) reinforced by R-GFs treated with detergent, and (4) reinforced by R-GFs treated with acetone

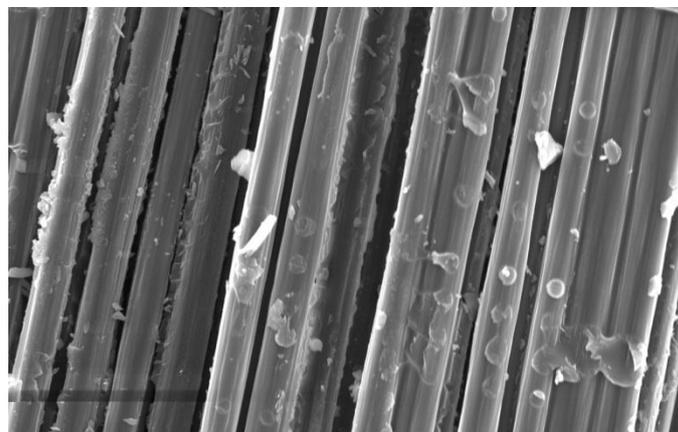
Figure 4-5 compares the bending strengths of V-GFRP (circle), R-GFRP reinforced by R-GFs (diamond), TR-GFRP reinforced by R-GFs treated with detergent (triangle), and TR-GFRP reinforced by R-GFs treated with acetone (square). The bending strength of R-GFRP was 26% that of V-GFRP (Fig. 4-5). The bending strength of TR-GFRP treated with detergent was slightly higher than that of R-GFRP, at 29% that of V-GFRP. The bending strength of TR-GFRP treated with acetone was nearly the same (94%) as

that of V-GFRP. Although the quantity and volume of nubble clinging to the surfaces of TR-GFs decreased, the bending strength of TR-GFRP treated with detergent improved only slightly. In contrast, that of TR-GFRP treated with acetone greatly improved. Acetone very effectively removed the unsaturated polyester resin impurities, although it cost more than detergent. To sum up, it was possible to obtain high-performance TR-GFRP by treating R-GFs with acetone.

4.3.2 Recycling CFRP and treating R-CFs

4.3.2.1 Surface morphology

The surface morphologies of R-CFs (Fig. 4-6 (a)) and V-CFs (Fig. 4-6 (b)) were examined by SEM (Fig. 4-6) at a magnification of 1000 \times . Many epoxy resin impurities could be observed on the surfaces of R-CFs, whereas V-CFs had cleaner, purer, and smoother surfaces. Epoxy resin impurities would spoil the interfacial adhesion between fibers and new resin when remanufactured into recycled CFRP (R-CFRP). As with R-GF, in order to obtain high-performance R-CFRP, surface treatment of R-CFs should be performed to improve interfacial adhesion.



(a)

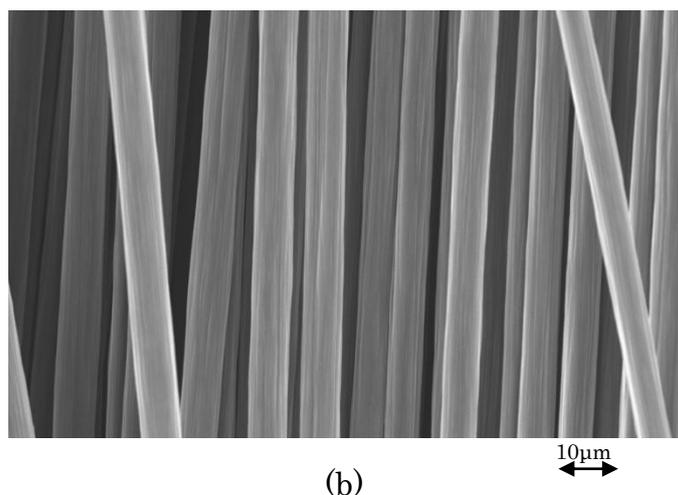


Fig.4-6 SEM micrographs of fibers at 1000× magnification, (a) R-CFs, (b) V-CFs.

Figure 4-7 (a) depicts the surface morphology of TR-CFs that were soaked in acetone for five days and cleaned by an ultrasonic washing machine for 1h after soaking. Figure 4-7 (b) illustrates the surface morphology of TR-CFs that were soaked in NMP at 200°C for three days and cleaned by an ultrasonic washing machine for 1h after soaking. All were analyzed at a magnification of 1000×. Many impurities were observed on the surfaces of the TR-CFs depicted in Fig. 4-7 (a). In contrast, fibers depicted in Fig. 4-7 (b) had clean, smooth surfaces. Although some nubbles were clinging to the surfaces of TR-CFs, their surfaces were nearly the same as those of V-CFs. The results of surface treatment indicated that acetone very effectively removed unsaturated polyester resin impurities but not epoxy resin impurities. However, NMP was very effective and possibly improved interfacial adhesion between fibers and new resin.

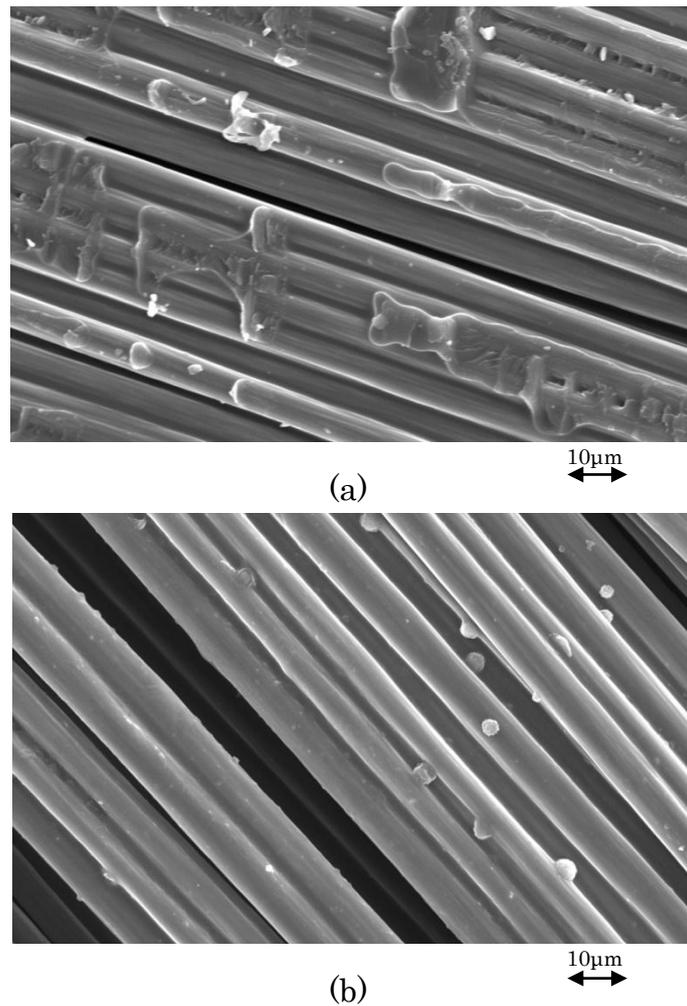


Fig. 4-7 SEM micrographs of TR-CFs at 1000× magnifications (a) acetone, (b) NMP.

4.3.2.2 Mechanical properties

Although the solutions effectively removed remaining epoxy resin impurities, whether the solutions would affect the fiber soaked in them was undetermined. Therefore, V-CFs were soaked in two different solutions and then fabricated to form treated virgin carbon fiber-reinforced polymer (TV-CFRP). The bending strength of TV-CFRP was measured and compared with that of V-CFRP.

Figure 4-8 compares the bending strengths of V-CFRP (circle), TV-CFRP reinforced

by virgin carbon fiber treated with acetone (triangle), and TV-CFRP reinforced by virgin carbon fiber treated with NMP at 200°C (square). The bending strengths of these three types of CFRP were nearly the same. Therefore, neither acetone nor NMP affected the bending strength of TV-CFRP. Based on the results presented in section 4.3.2.1, NMP could be considered as a solution for removing epoxy resin impurities in the future.

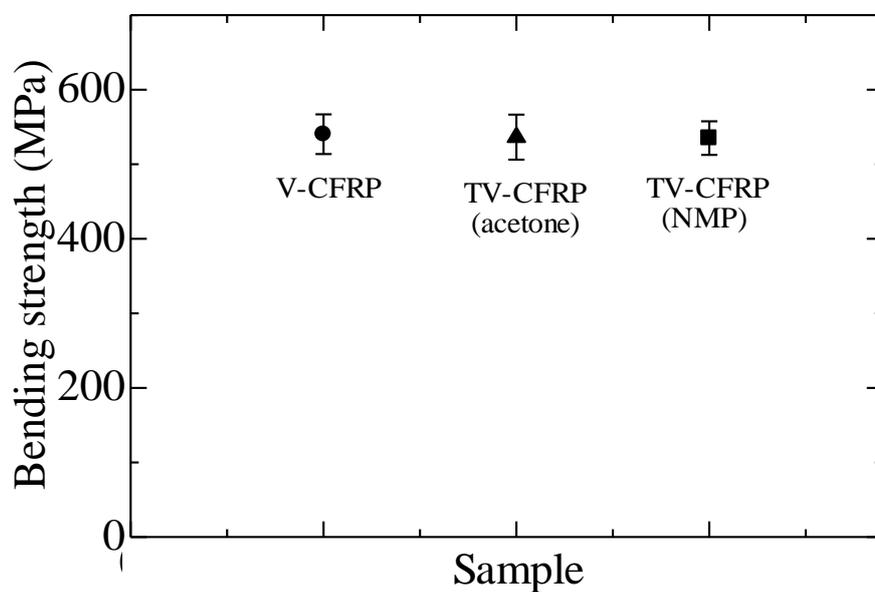


Fig. 4-8 Bending strength of V-CFRP and TV-CFRP (1) reinforced by V-CFs, (2) reinforced by V-CFs treated with acetone, and (3) reinforced by V-CFs treated with NMP.

The results presented in section 4.3.2.1 indicated that NMP effectively removed epoxy resin impurities. Although it was determined that acetone did not effectively remove epoxy resin impurities, it was not determined whether bending strength would be improved by acetone or NMP, and how much it would be improved. Therefore, the bending strengths of V-CFRP, R-CFRP, and TR-CF reinforced polymer (TR-CFRP)

were measured (Fig. 4-9).

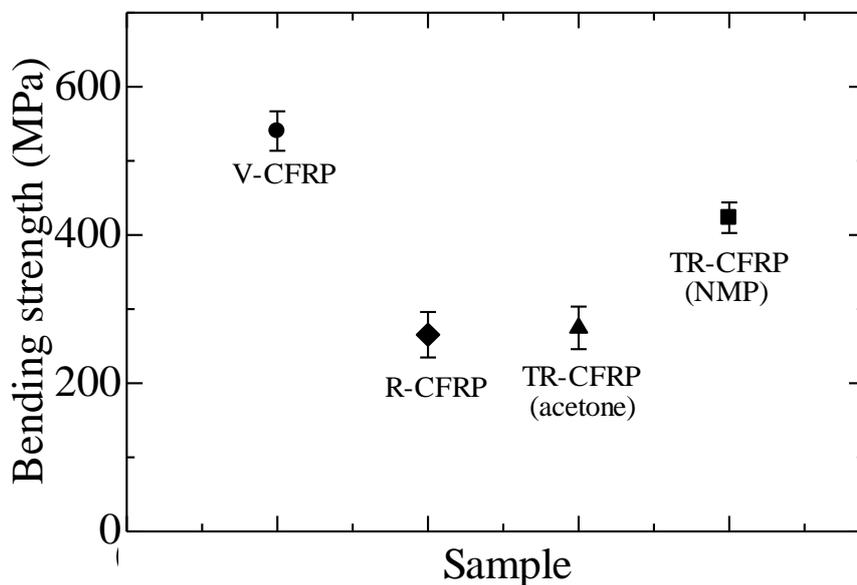
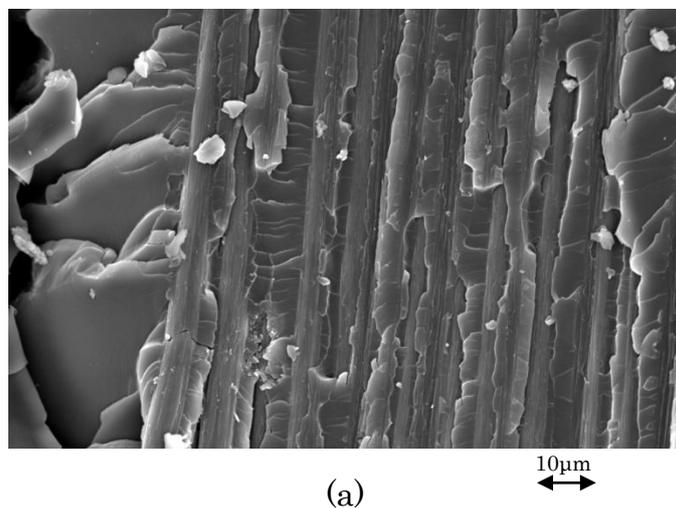


Fig. 4-9 Bending strength of V-CFRP, R-CFRP and TR-CFRP (1) reinforced by V-CFs, (2) reinforced by R-CFs, (3) reinforced by R-CFs treated with acetone, and (4) reinforced by R-CFs treated with NMP

Figure 4-9 compares the bending strengths of V-CFRP (circle), R-CFRP reinforced by R-CFs (diamond), TR-CFRP reinforced by R-CFs treated with acetone (triangle), and TR-CFRP reinforced by R-CFs treated with NMP at 200°C (square). The bending strength of R-CFRP was 49% that of V-CFRP (Fig. 4-9). The bending strength of TR-CFRP treated with acetone was 51% that of V-CFRP. The bending strength of TR-CFRP treated with NMP at 200°C was 78% that of V-CFRP. Bending strength was thus significantly improved by treatment with NMP. NMP very effectively removed epoxy resin impurities, and it was possible to obtain high-performance TR-CFRP by treating R-CFs with NMP. Although NMP costs more than acetone, if the R-CFs can be reused in high-value TR-CFRP, it is still a significant solution for treating R-CFs.

Compared to TR-GFRP, amount of improved bending strength distinctly fall in the case of TR-CFRP could be ascribed to not only poor adhesion between epoxy resin impurities on CF and resin but also poor adhesion between CF and resin. This explanation was supported by observations made under the SEM and shown in Fig. 4-10, where the features on the fracture surface of failed samples shown was demonstrated. The V-CFRP showed good river patterns in the resin-rich regions and considerable resin adherence to the CF (Fig. 4-10(a)). TR-CFRP, on the other hand, didn't show a bundle of fibers with considerable resin adherence (Fig. 4-10(b)). Some regions showed rough CF stained with epoxy resin impurities, meanwhile, some regions showed hardly any smearing of resinous material and smooth CF. Furthermore, if the bending strength needed to be improved, other methods could be considered, such as plasma treatment, coupling agents and so on.



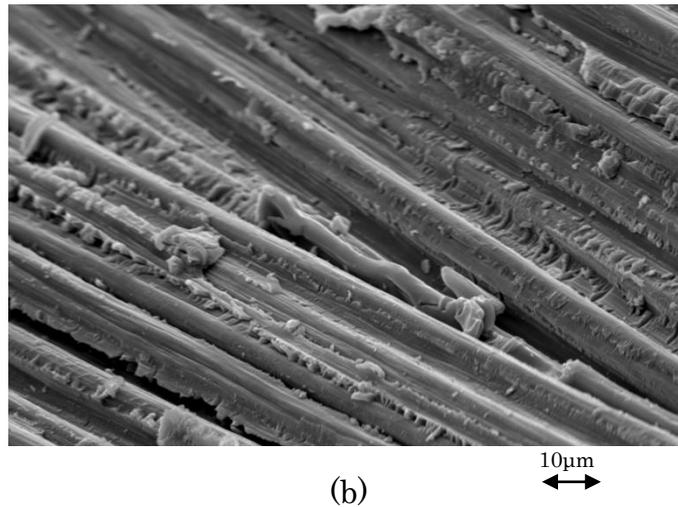


Fig. 4-10 SEM micrographs of fracture surface of samples at 1000 \times magnification (a)

V-CFRP, (b) TR-CFRP

4.4 Summary

In chapter 4, R-GFs were treated with detergent and acetone, and R-CFs were treated with acetone and NMP. The bending strengths of FRP reinforced with treated recycled fibers were evaluated, and the effect of solutions on surface treatment and bending strength was determined. The following conclusions can be drawn from the present investigations.

(1) It is possible to recycle reinforced fibers from FRP, and to remanufacture them into high-value R-FRP for reuse.

(2) Acetone effectively removes unsaturated polyester resin impurities, with no adverse effect on the bending strength of TV-GFRP. The bending strength of R-GFRP could be dramatically improved (from 26% to 94%) through treatment with acetone. NMP effectively removes epoxy resin impurities, with no adverse effect on the bending strength of TV-CFRP. The bending strength of R-CFRP could be significantly improved (from 49% to 78%) through treatment with NMP.

The price of reinforced fiber, especially CFs, is very high. If reinforced fiber can be recycled and remanufactured into TR-FRP with as high a performance as possible, the value of TR-FRP will be greater than the recycling cost, and the recycling of FRP can be carried out continuously without assistance from government. These results increase the probability that this method will be widely used in the future.

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CHAPTER FIVE

Low-velocity impact response and compression after impact assessment of recycled fiber reinforced plastic composites

Chapter5 Low-velocity impact response and compression after impact assessment of recycled fiber reinforced plastic composites

5.1 Introduction

Carbon fiber (CF) is one of the most widely used reinforcing fibers for composite materials. Since its commercial introduction in 1970, it has found increasing usage in aerospace, military, automobile, and sports goods industries, owing to its specific strength, specific modulus, and thermophysical properties. The global demand for PAN-based CFs grew to over 30,000 tons by 2010, and it is expected to rise to 50,000 tons by 2013.

CFs are usually combined with other materials to form a composite. When combined with a polymer resin and molded, it forms CFRP which has a very high strength-to-weight ratio, and is extremely rigid although somewhat brittle. However, the challenge of separating CFRP into elemental components has raised a concern regarding its disposal during its end-of-life cycle. CFRP disposal is usually performed by incinerating or landfilling without any recycling [1, 2]. Recycling technology has been studied extensively in recent years, and various methods [3-9] have been investigated. Also under consideration are viable ways to utilize recycled CFs (e.g., concrete filler [10] dough molding compound (DMC) reinforcement [3], injection molded thermoplastic composites [11], and electromagnetic interference shielding [12]). However, the strong connection among recycling, remanufacturing, and the final performance of recyclates [13] clearly affects the types of market in which recycled CFs

can be introduced, and thus greatly impacts any commercial recycling operation. Processes, performance, commercialization, and markets must therefore be considered in the comprehensive analysis of CFRP recycling operations [14].

There are many published technologies about CFRP recycling. From these reports, fibers could be recycled by all these technologies, but recycled fibers were short and in disorder, and the strength reduced too. So the value is still low and need support of government. Until now, there was no research for recycling and reusing long CFs. We considered CFRP to be the most valuable pattern (There are many pattern for reusing CFs, e.g. nonwoven, short fiber fill to thermoplastic for injection molding, the value is extraordinary lower than long fiber) using long CFs to reuse high-performance recycled CFs, leading to a sustainable recycling system without support of government. Thus, we developed a new recycling technology using a steam system. Our previous studies [15-17] indicated that recycling CFRP using superheated steam is optimal, making it possible to obtain long fibers with little degradation of tensile strength, and we developed a surface cleaning method by which the bending strength of TR-CFRP composites was improved up to 80% that of V-CFRP. Unfortunately, the impact response and CAI of TR-CFRP and R-CFRP are still unknown. If recycled CFs are reused as CFRP, they may suffer damage during manufacturing, assembly, and maintenance, due to different types of impact. One main difficulty with fiber-reinforced polymer composites is that their performance degrades once they are subjected to an impact of even modest magnitude. The impact event typically causes matrix cracking, fiber breakage, and delamination within the structure. Delamination is probably the most serious problem, given the difficulty of its visual detection and the extent to which it degrades mechanical properties [18]. The greatest degradation is that of the

compression strength [19], which may be 40 to 60% that of an undamaged structural element [20]. Therefore, damage resistance is an important factor in the design of fiber-reinforced polymer composites. Damage resistance in laminates is usually studied by determining the effect of different impact energies on residual strength. The compression after impact (CAI) test is an experimental test of components damaged by low-energy impact.

Evaluating the CAI of a damaged structure is important for practical and effective damage-tolerant design. Compared with undamaged specimens, impact-damaged laminates experience more significant strength reductions when loaded in compression, due to local instabilities arising from existing damage. For future applications of recycled carbon in many fields, it is necessary to investigate the influence of recycling on CAI strength and related damage mechanisms. When impact energy is high, impact-induced delamination is large, resulting in a greatly weakened composite structure. CAI strength decreases with increasing impact-induced delamination area [21, 22]. Closer study at each impact energy level provides important information for future applications.

In this study, we conduct detailed numerical analysis of the CAI responses of V-CFRP, R-CFRP, and TR-CFRP. The damage resistance of these three laminates was investigated. The residual strength was obtained and examined to determine how it is modified by changes in impact energy. These results were used to evaluate the effect of surface cleaning and provide the basis of future applications.

5.2 Experiments

5.2.1 Specimens

Three kinds of specimen were used for the study. There were three types of CF and one epoxy resin. Virgin CFs (Torayca ® plain woven fabric) were purchased from Toray Industries, Inc., and recycled CFs were obtained from V-CFRP, which decomposed immediately after molded, through a superheated steam process developed by our lab[15, 16]. Treated recycled CFs were with a surface cleaning process. Recycled plain woven fabric carbon fibers were fixed by wire netting and soaked in solution to keep them in order. They were soaked in NMP (Kanto Chemical, Japan) for 3 days at 200 °C. They were then cleaned by an ultrasonic washing machine for 1 h [17]. It could be understood as there are three parts of V-CFRPs. One part of V-CFRPs were tested in impact. One part of V-CFRPs were decomposed by superheated steam, and recycled carbon fibers (R-CFs) were remolded by VaRTM, molded composite plates were called recycled carbon fiber reinforced polymer(R-CFRP), then they were tested in impact. The last part of V-CFRPs were decomposed by superheated steam, R-CFs were surface treated, and the carbon fibers called TR-CFs. They were remolded by VaRTM, molded composite plates were called treated recycled carbon fiber reinforced polymer (TR-CFRP), and then they were tested in impact. Details could be found in Fig. 1. The recycled CFs were not resized after recycling. Thermosetting epoxy resin (XNR6815) obtained from Nagase ChemteX Corporation was used as the matrix of CFRP. Hardener (XNH6815) was also purchased from Nagase ChemteX Corporation. Epoxy resin and hardener were 100 and 27 parts by weight. The eight-ply CFs woven fabrics with sequence of $[0^\circ/90^\circ]_2s$ employed for the tests were manufactured by vacuum-assisted resin transfer molding (VaRTM). For the curing process, laminated plates were retained

at a constant pressure (approximately one atmospheric pressure) and room temperature for 24h. Cured samples were cut into rectangular specimens (80×50×2.5mm) to meet the strict dimension requirements specified in the supplement of JIS K7089, which apply to smaller and thinner specimens. The fiber volume fraction of laminated composite plate is approximately 46%.

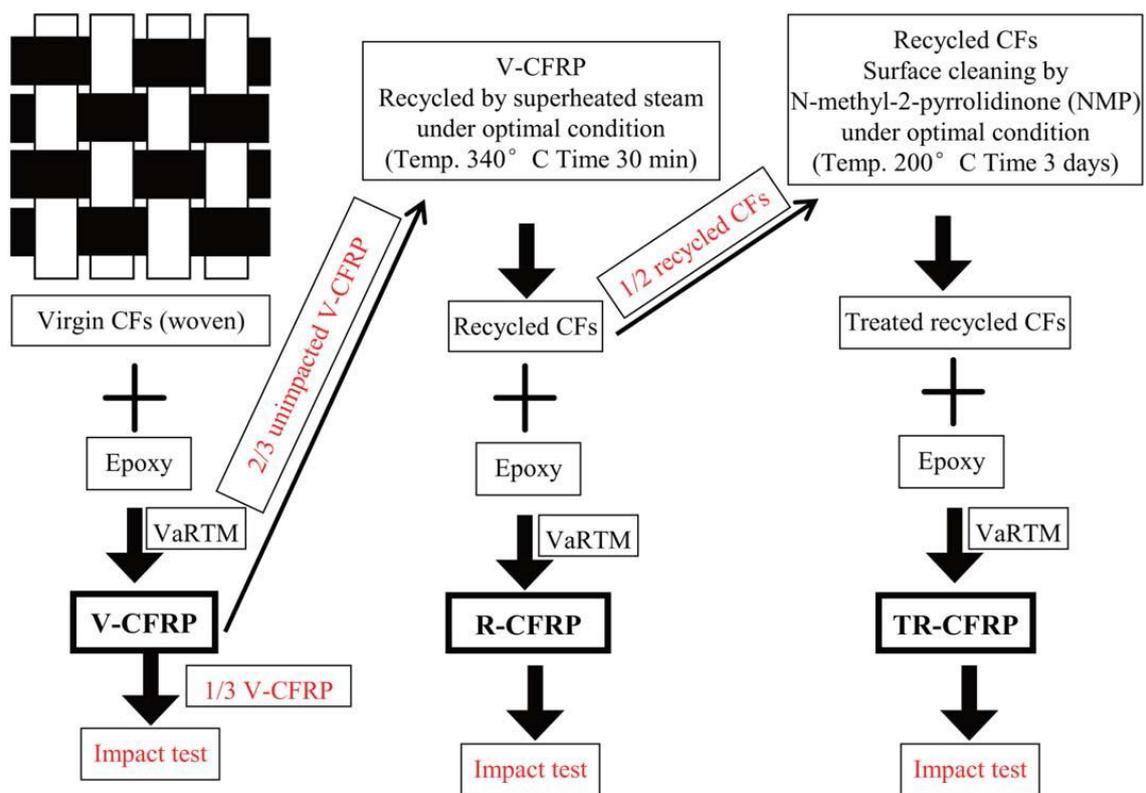


Fig. 5-1 Schematic diagram of specimen preparation

5.2.2 Impact Testing

Impact testing was conducted using a Charpy impact tester (D-7900 type 510L 100/00, Zwick GmbH & Co. KG) that had a spherical impact head with a 5mm radius of curvature. The apparatus consisted of a pendulum with a defined mass attached to a rotating arm pinned to the machine body, an acceleration transducer (Kyowa Electronics,

Inc., AS-1000HA) attached to the pendulum to measure change of acceleration in the impact process, and an anvil supporting the specimen [23]. At the center of anvil here was a hole, where is the same with impact location of specimen. Specimen was clamped on the anvil use an iron sheet with oblong hole, size of which was smaller than specimen, and firmly fixed use fore screws as Fig. 2. Clamping could be considered as a real rigid fixation. Then pendulum was raised to a desired angle, then fell following a circular trajectory, and hit the center of the specimen, transferring kinetic energy to it. Rebound was avoided by catching the pendulum when it bounced back after hitting specimen. The pendulum had a mass of 1.285kg and a swing arm length of 390mm. Energy losses due to bearing friction and air resistance were disregarded, due to their small contribution to the energy balance. All specimens were subjected to impact tests. The energy levels for the impact test were set as 0.5/1.0/1.5/2.0J/mm. Five specimens were tested for each energy level. The acceleration transducer measured the change of acceleration, which was recorded by bridge unit control software (Kyowa Electronics, Inc., DBU-120A).

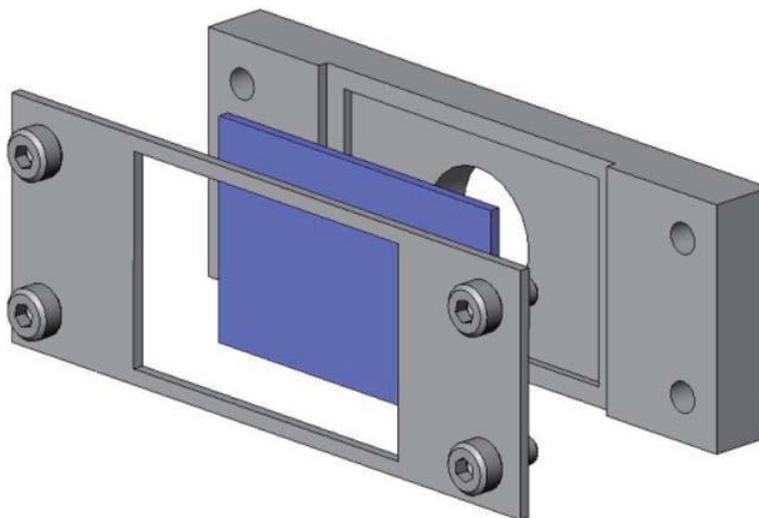


Fig. 5-2 Schematic drawing of clamping conditions

5.2.3 Damage Inspection

After impact testing, damage evolution was inspected from the side opposite the impact side of specimens by ultrasonic scanning (FineSAT FS100S, Hitachi Engineering & Services Co., Ltd.) using a 15MHz transducer in pulsed-echo mode. This system can provide the plane-view of accumulated delamination by processing ultrasonic echo data and probe locations. After ultrasonic inspection, the impact side, opposite side, and profile side of the specimens were observed using photography. Some of the specimens were then cut into slices near their center using a fine diamond saw. Each cross-section was ground and polished using a precision polishing machine (SCANDIMATIC 33305, SCAN-DIA GmbH & Co. KG). The mirror-finished cross-section was observed by scanning electron microscopy (SEM) (InTouchScope JSM-6010LA, JEOL, Ltd.).

5.2.4 Compression after Impact

CAI testing was employed to evaluate the damage resistance of specimens. This widely used test measures the residual compressive strength (RCS) of composites with impact damage. RCS is sensitive to this type of damage due to localized buckling of sublaminates created by delamination, leading to stress concentration around the region of reduced stiffness [24]. CAI tests were performed at room temperature, using a mechanical property test machine (TMI UTM-10T; Toyo. Baldwin Co., Ltd.) with a loading cell of 100kN, and the CAI device developed for this study. Since the CAI test results were especially sensitive to fiber orientation relative to loading direction, special care was taken during sample cutting so as to insure that the top and bottom edges of the samples were parallel with each other and perpendicular to the loading axis. The

specimens were compressed at a constant displacement rate of 0.5mm/min, following JIS K7089. Twenty-five specimens of each type (V-CFRP, R-CFRP, and TR-CFRP) were tested: five unimpacted specimens and five impacted specimens at each energy level (0.5/1.0/1.5/2.0J/mm) in order to compare the loss of residual strength caused by impact damage.

Data sets of load force and displacement were obtained at a rate of 10 data sets per second. From these data sets, the maximum failure force of the specimen was obtained to evaluate CAI strength. The maximum compression strength or CAI strength is calculated by equation (1):

$$\sigma_{ULT} = \frac{P}{bt}, \quad (5-1)$$

where σ_{ULT} is the ultimate compression strength, P is the ultimate compression load, b is the average width, and t is the average thickness.

5.3 Results and discussion

5.3.1 Morphology of Recycled CF Fabrics

State of recycled CF fabrics was investigated. The original weaving structures of recycled CFs and treated recycled CFs were preserved. They were the same as virgin CFs (Fig. 5-3). The recycled CFs were not broken after recycling process. However, the tensile strength of recycled CFs dropped slightly, which is about 5% lower than virgin CFs. The fineness of the yarns was 198tex and it didn't change after recycling. The warp ends and fill picks of recycled CF fabrics were all 12.5counts/25mm, and they were almost the same with virgin CF fabrics. Residual epoxy resin of recycled CFs was observed by SEM (Fig. 5-4), which were recycled at a temperature of 340 °C for 30 min[16].

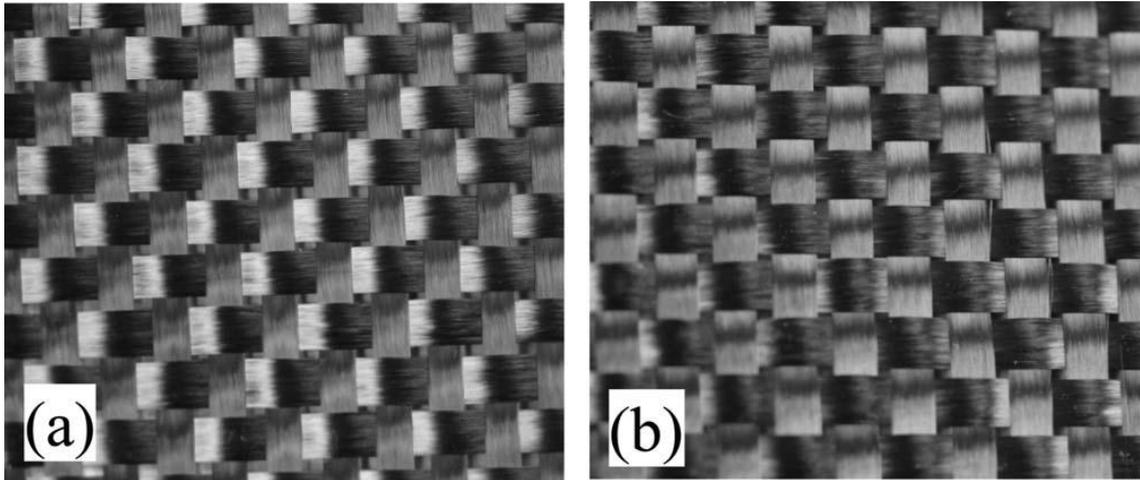


Fig. 5-3 Photograph of CFs. (a) Virgin CFs; (b) recycled CFs.

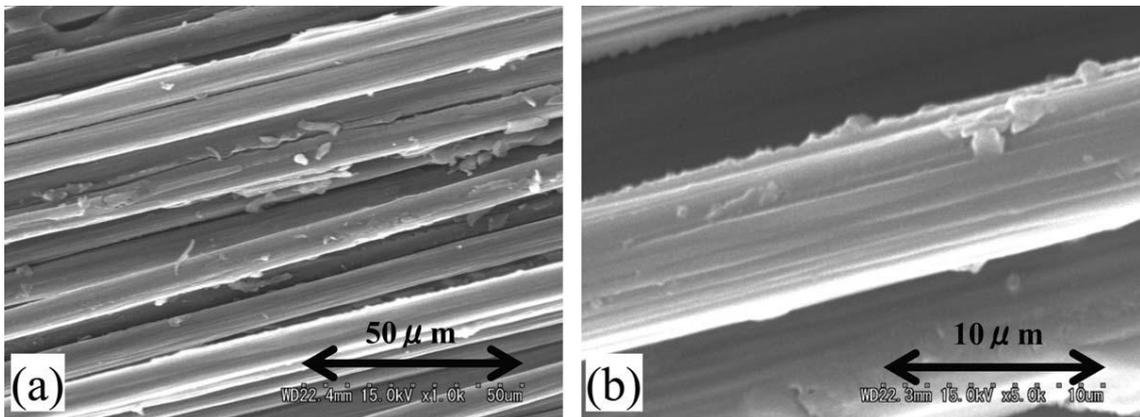


Fig. 5-4 SEM micrographs of recycled CFs. (a) at 10003 magnifications; (b) at 50003 magnifications.

5.3.2 Characteristic Impact Loads

Very smooth load versus time plots of three laminate types for representative impact levels are plotted in Fig. 5-5. The impact damage resistance of a material can be characterized in terms of incipient damage load (P_i) and maximum load (P_m) [25, 26]. The incipient damage load, or the first failure point [27], can be identified by the first sudden load drop and/or change in slope in the ascending portion of the load, as a consequence of interface failure or matrix cracking near the back surface of the laminate.

Beyond the incipient damage load, the residual strength can be influenced significantly by impact energy, due to damage growth within the laminate. P_m represents the peak load value that a composite laminate can tolerate under a particular impact level before undergoing major damage [26, 28].

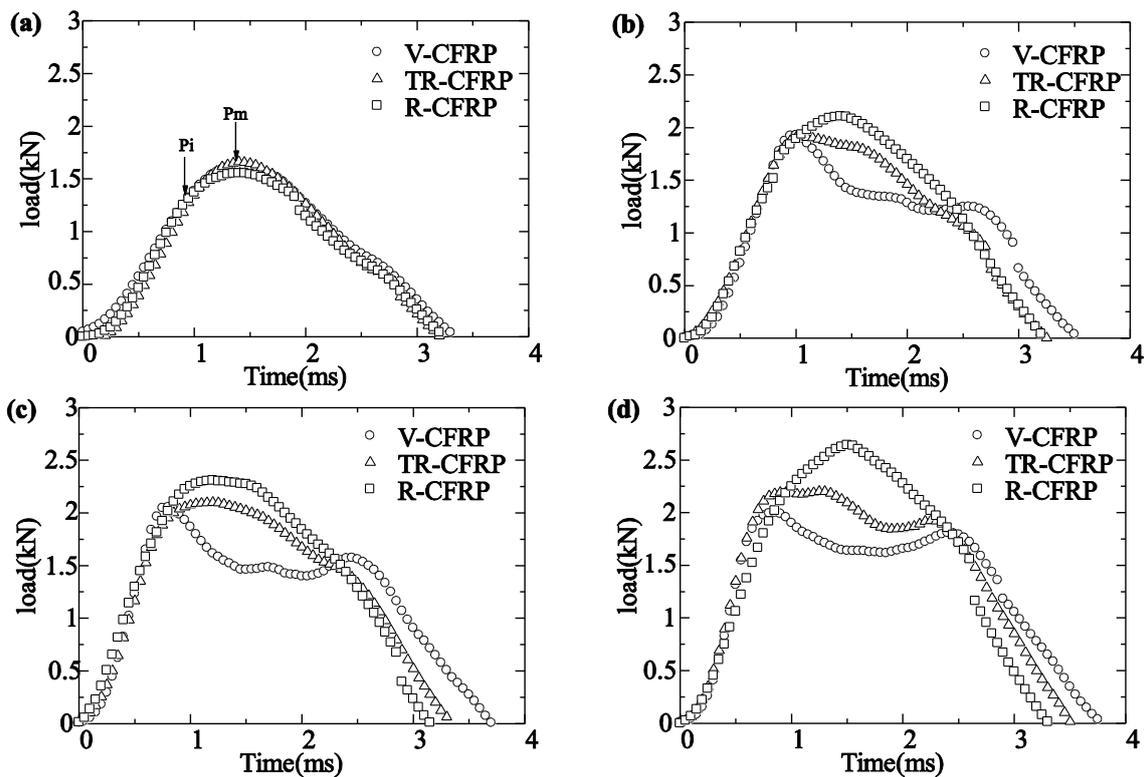


Fig. 5-5 Load vs. time responses for (a) 0.5J/mm, (b) 1.0J/mm, (c) 1.5J/mm, and (d) 2.0J/mm impact energies

Upon impact, energy is absorbed by a material through elastic or plastic deformation and through creation of new surfaces through failure. Very little or no plastic deformation occurs with CFRP. Impact energy is initially absorbed through elastic deformation up to a threshold energy value. At and beyond that value, impact energy is absorbed through both elastic deformation and creation of damage through various

failure modes (e.g., delamination, fiber breakage, matrix crack, and splitting) [29].

It is possible to observe three different types of curve in Fig. 5-5. Curve of V-CFRP varies from one (Fig. 5-5 (a)) peak to two peaks (Fig. 5-5 (b), Fig. 5-5 (c) Fig. 5-5 (d)). Curve of TR-CFRP also varies from one (Fig. 5-5 (a)) peak to two peaks (Fig. 5-5 (b), Fig. 5-5 (c) Fig. 5-5 (d)). Curve of R-CFRP only one peak in this test. For the impact level of 0.5J/mm, there is only one broad peak, which could be related to initial failure due to interface failure and matrix cracking near the back surface of the laminate. For the other two impact levels (1.0J/mm and 1.5J/mm), two peaks occur in V-CFRP; the first one signifies initial failure, and the second one represents crack growth from the initial failure, leading to fiber failure. In this case, the impact energy overcomes the residual strength of the laminate [30]. No clear second peak occurs in TR-CFRP. Instead, the curve is in the shape of a plateau, where initial failure and crack growth merge. In Fig. 5-5 (d), the second peak forms, representing failure modes other than initial failure, due to increasing impact energy. In Fig. 5-5, there is only one broad peak in R-CFRP for all impact levels, indicating that major impact damage is the result of initial failure of delamination.

For discussing the mechanism of impact, the section of impacted area was observed by SEM (Fig.5-6). From the Fig. 5-6 (a), we can see fiber failure in both energy levels, which represent two peaks curve in Fig. 5-5 (c) and (d). From the Fig. 5-6 (b), we can see both fiber failure and delamination. The fiber failure in case of 2J/mm is more obvious than that in case of 1.5J/mm, which represent a shape of a plateau in Fig. 5-5(c) and two peaks curve in Fig. 5-5(d). From the Fig. 5-6 (c), we can only see delamination in both levels, which represent one peak curve in Fig. 5-5 (c) and (d). From the comparison of Fig. 5-5 and Fig. 5-6, one peak curve represents initial if the impact

energy smaller than the residual strength of the laminate (the case of 0.5J/mm) or delamination if the impact energy beyond the residual strength of the laminate (the case of 1J/mm, 1.5J/mm, 2J/mm of R-CFRP). Two peaks curve represents fiber failure. In the cases of 1J/mm, 1.5J/mm, 2J/mm of V-CFRP, there are two peaks in the curve. In these cases of TR-CFRP, we can see quasi two peaks curve in Fig. 5-5 (b) and (c), and two peaks curve in Fig. 5-5 (d). Surface clean makes the impact property of TR-CFRP is similar as V-CFRP, and is different to R-CFRP. The surface cleaning effectively improved interfacial adhesion between fibers and new resin.

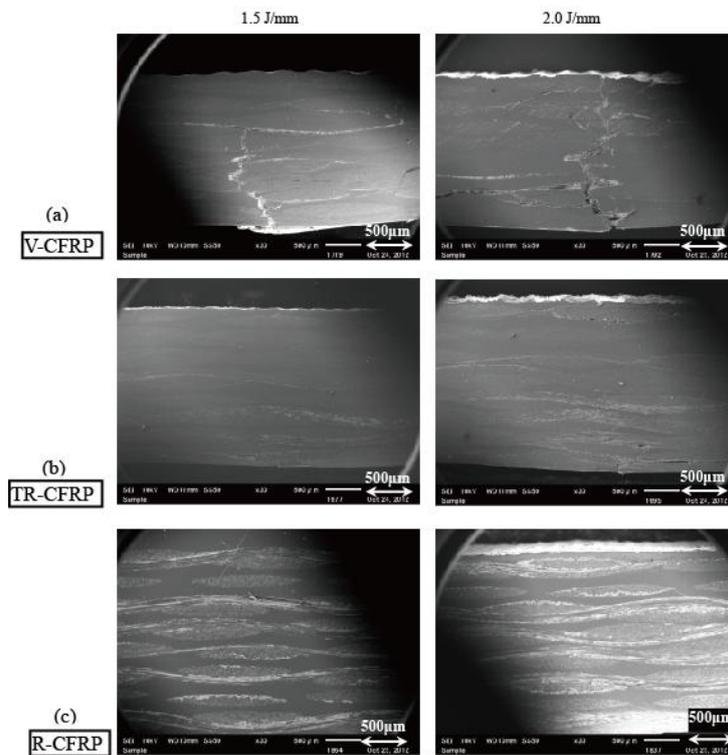


Fig. 5-6 SEM images of section of the impact area. All specimens impacted at the impact energy level of 1.5J/mm and 2J/mm. (a)V-CFRP. (b) TR-CFRP. (c) R-CFRP

Figure 5-7 plots the impact parameters of peak load and time to peak load. Maximum load increases with impact energy level for all the laminates with the exception of

V-CFRP. For V-CFRP, maximum load increases with impact energy up to 1.0J/mm, beyond which it is almost constant. It seems that V-CFRP cannot withstand dynamic peak load beyond 2kN, due to back surface splitting. Time to peak load decreases with increase in impact energy level, with the exception of R-CFRP. For R-CFRP, the time to peak load is almost constant and the maximum load increases with impact energy, indicating that the major impact damage is delamination damage.

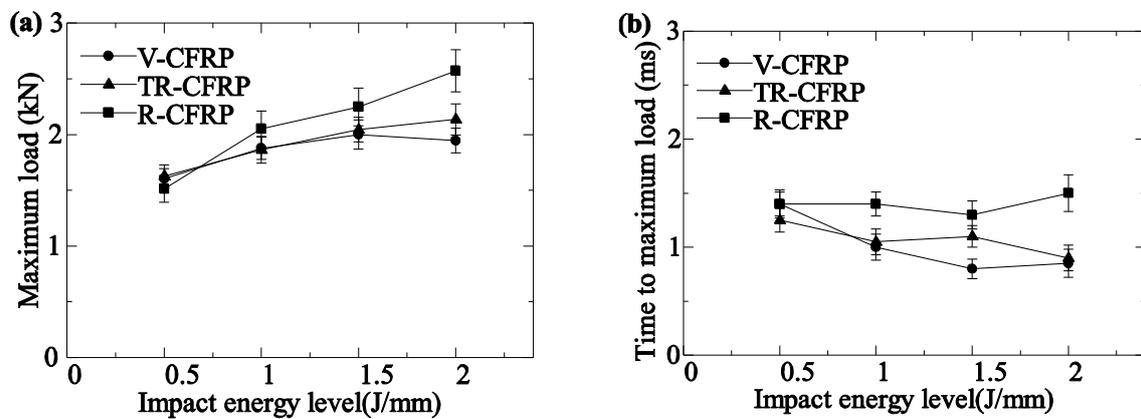


Fig. 5-7 Relationship between (a) maximum load versus impact energy level and (b) time to maximum load versus impact energy level

As reported elsewhere [27], woven fabric composites (V-CFRP in this study) do not exhibit any delamination damage under low-velocity impact. From above, in the case of 0.5J/mm, the impact energy smaller than the residual strength of the laminate, the impact load was the same. The impact load of V-CFRP and TR-CFRP was lower than that of R-CFRP accompanied with two peaks curve, which mean fiber failure occurred. Fiber failure could absorb more energy than delamination, result in lower impact load. So the impact load of V-CFRP and TR-CFRP was lower than that of R-CFRP when impact energy beyond the residual strength of the laminate. For R-CFRP, energy was

used not to create penetration or back surface damage, but to develop delamination damage due to bad adhesion. In the case of R-CFRP, there was only delamination occurred, and absorbed a little energy, result in high value impact load. Poor fiber-resin adhesion result in delamination occurred easier than fiber failure. Fiber-resin adhesion was improved by surface cleaning, so impact load of TR-CFRP is among V-CFRP and R-CFRP.

5.3.3 Characterization of Impact Damage

Figure 5-8 presents typical ultrasonic C-scan images of unimpacted specimens (0J/mm), which were scanned for comparison, and impacted (0.5J/mm, 1.0J/mm, 1.5J/mm, and 2.0J/mm) specimens. All pictures are the same for all specimens. The white region at the center of an image represents the delamination area induced by low-velocity impact. Delamination size obviously increases with increasing impact energy for all cases. For V-CFRP, almost no white area occurs at the center of the image with 0.5J/mm, indicating that almost no delamination damage is created by impact. The white area increases with increasing impact energy level to a cross shape with a cross split inside (Fig. 5-9 (a)). This indicates that only a little delamination damage occurs under low-velocity impact for V-CFRP. This result was the same as impact load, and showed correctness of information gained from impact load curve. The cross split can be considered as splitting failure mode near the back surface, as confirmed in Fig. 5-10 (a). For TR-CFRP, no white area is observed with 0.5J/mm. Its size also increases with impact energy level, so that with 2.0J/mm, the white area has a cruciform shape, similar to that for V-CFRP. An indistinct cross split can be seen inside the cruciform (Fig. 5-9 (b)). For R-CFRP, even at the lowest impact energy level, a white area is obvious at the

center of the image. This white area is circular at 0.5J/mm; it changes with increasing impact energy level, so that at 2.0J/mm, it is like a four-leaf clover (Fig. 5-9 (c)), which occupies most of the image. This indicates much delamination, which reduces the residual strength of the specimens.

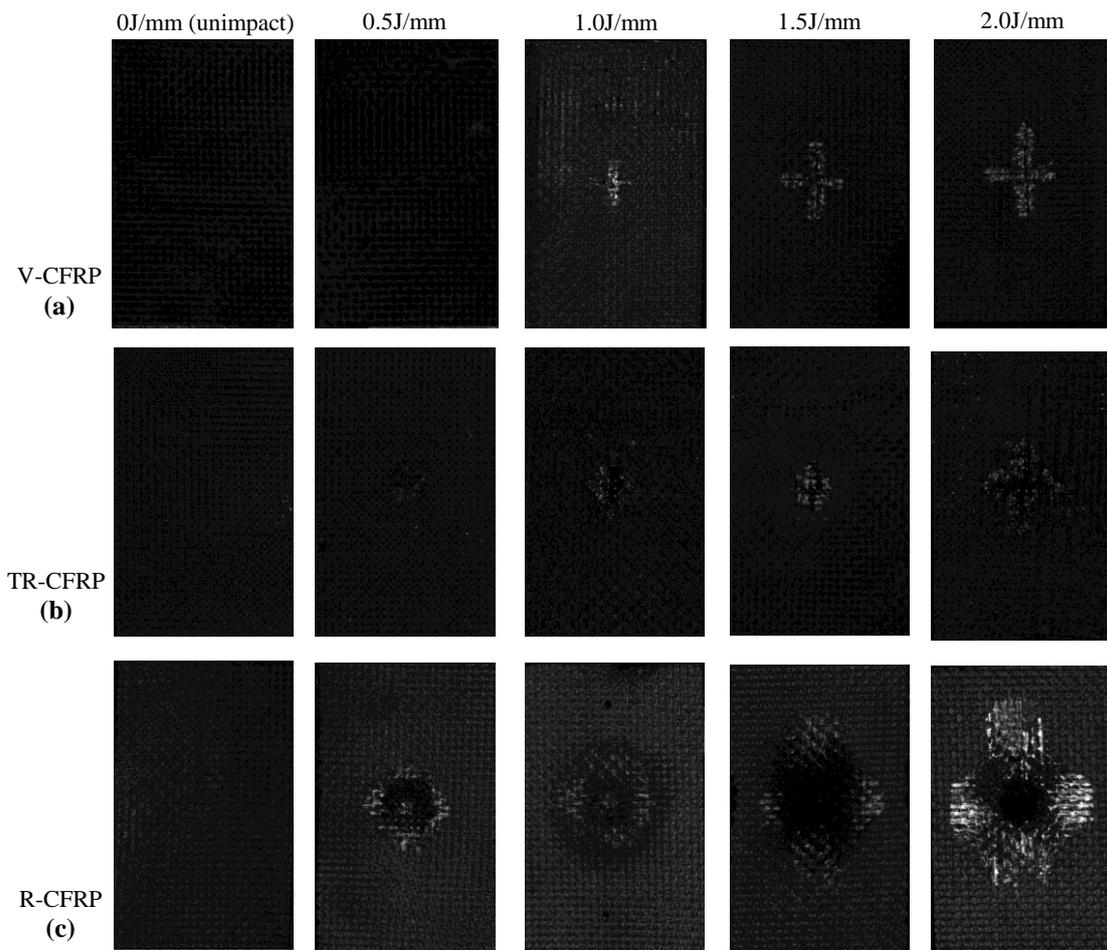


Fig. 5-8 Ultrasonic C-scan images of three specimen ((a) V-CFRP, (b) TR-CFRP, (c) R-CFRP) at impact energy levels of 0J/mm, 0.5J/mm, 1.0J/mm, 1.5J/mm, 2.0J/mm

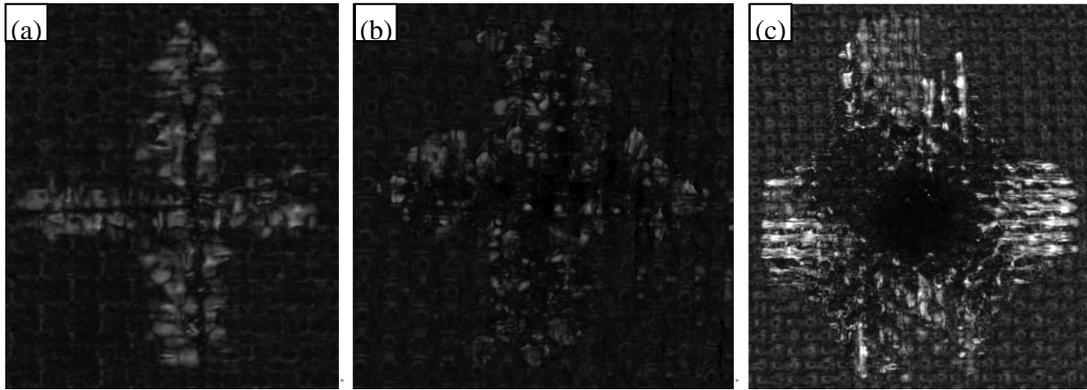


Fig. 5-9 Center white area of ultrasonic C-scan images for 2.0J/mm: (a) V-CFRP, (b) TR-CFRP, (c) R-CFRP

From the result of section 5.3.2, we know that impact loaded to fiber failure in the case of V-CFRP, a little delamination and fiber failure in the case of TR-CFRP, and only delamination occurred in the case of R-CFRP. From the result of ultrasonic C-scan images, we can confirm that delamination also existed in the case of V-CFRP, and the delamination area of R-CFRP is the biggest of all. Fiber-resin adhesion of R-CFRP is very bad [17], so it is could be considered that bad fiber-resin adhesion loaded to delamination occurred easily. Good fiber-resin adhesion loaded to fiber failure occurred easily. Surface cleaning loaded to improvement of impact property of TR-CFRP, due to improved fiber-resin adhesion.

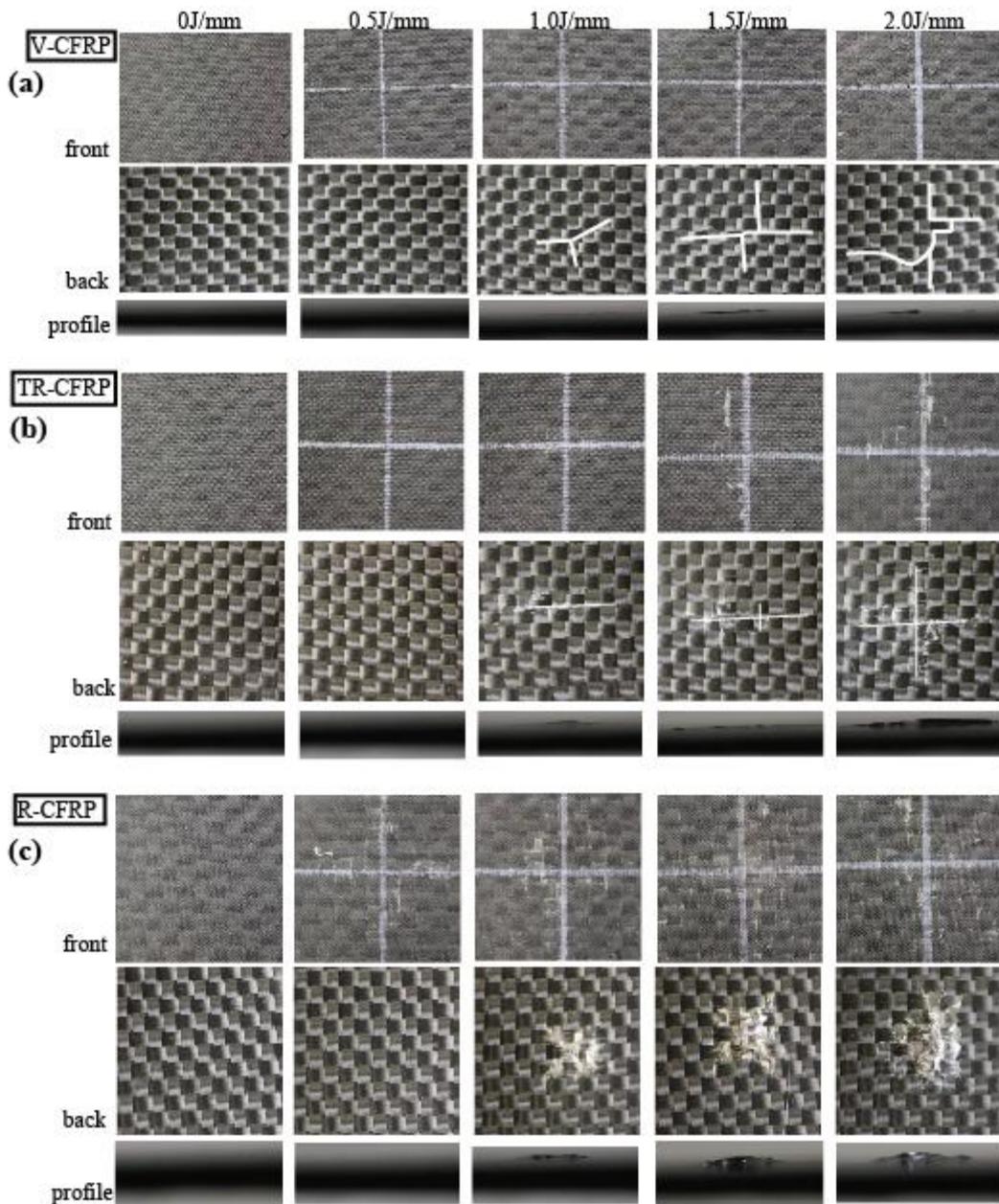


Fig. 5-10 Photographs of the front, back, and profile surfaces of three specimens ((a) V-CFRP, (b) TR-CFRP, (c) R-CFRP) subjected to various impact energy levels of 0J/mm, 0.5J/mm, 1.0J/mm, 1.5J/mm, and 2.0J/mm

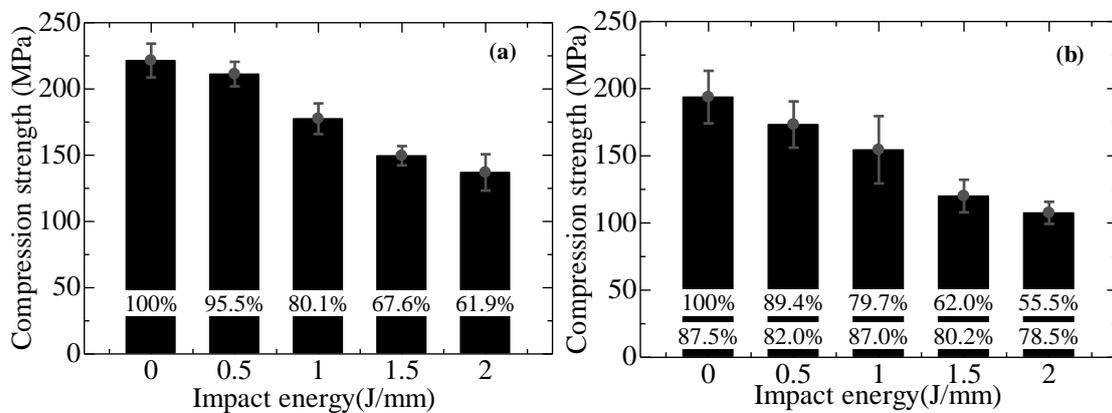
Among the three specimens, V-CFRP had the most resistance to impact. For all

impact energy levels, only horizontal and vertical back surface cracks were created in V-CFRP specimens, and nearly no damage occurred at the impact surface (Fig. 5-10 (a)). From the profile side, prominent back-surface cracks could be confirmed. When the V-CFRP was impacted at the lowest level, the results were almost the same as with the unimpacted specimens. No influence was observed at 0.5J/mm. Back-surface cracks developed into faint horizontal and vertical splitting with 2J/mm (Fig. 5-10 (b)). Small quantity cracks were observed on the front side with more prominence than for the V-CFRP specimens. Finally, no cross shape cracks occurred on the back side of the specimens (Fig. 5-10 (c)); instead, circular cracks occurred. Obvious short cracks were observed on the front surface for all impact energy levels. The crack area was generally much larger on the back surface than on the front surface. The larger damage area on the back surface indicated extensive delamination.

5.3.4 CAI Strength and Failure Mechanisms during CAI Tests

The bar charts in Fig. 5-11 indicate CAI strength versus impact energy level, and the error bars represent one standard deviation. To clarify the influence of recycling on CAI strength, Fig. 5-11 includes data of compression before impact (CBI) as the impact energy level of 0J/mm. In Fig. 5-11 (a), the percentage represents the retentive strength rate (R_i), which is the ratio of CAI strength of each impact energy level to CBI strength. In Figs. 5-11 (b) and (c), the first line percentage is the same as (a), and the second line percentage (R_o) is the repaired strength rate, which is the ratio of the strength of each impact energy level to that of the corresponding impact energy level of V-CFRP. As expected, specimens exhibit a similar trend: An increase in damage area with increasing impact energy is matched by a reduction in CAI strength. The trend of a reduction in

CAI strength is similar to the above observation of impact damage. Figure 5-11 (a) indicates no obvious influence at the lowest impact energy level. CAI strength drops suddenly beyond the impact energy level of 1J/mm. R_i of TR-CFRP is 5%-10% lower than that of V-CFRP, whereas R_i of R-CFRP is 10%-15% lower than that of V-CFRP. It may attribute to the surface of carbon fiber, which is more apparent for R-CFRP. R_o of TR-CFRP is almost 80%, whereas that of R-CFRP is 50%. The effect of surface cleaning evaluated by CAI testing is almost the same as that evaluated by bending strength [17]. From the results of section 5.3.2 and 5.3.3, impact resulted in fiber failure and a little delamination in the case of V-CFRP. Both delamination and fiber failure formed in the case of TR-CFRP, delamination was a little much than V-CFRP. Only delamination occurred in the case of R-CFRP. Fiber-resin adhesion was weak in the case of R-CFRP. Bad fiber-resin adhesion resulted in much delamination under impact load. Delamination caused reduction of CAI strength. Fiber-resin adhesion was improved by surface cleaning, so the CAI strength of TR-CFRP was higher than that of R-CFRP. Due to reduction of tensile strength of recycled fiber [16] and delamination, CAI strength of TR-CFRP was lower than that of V-CFRP.



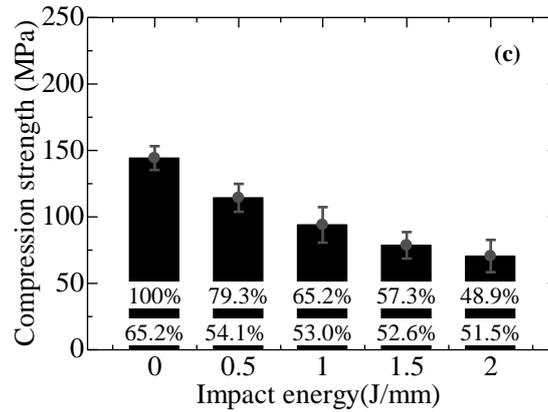


Fig. 5-11 Relationship between CAI strength and impact energy level of composite laminates. (a) V-CFRP. (b) TR-CFRP. (c) R-CFRP

Figure 5-12 presents photographs of the profile side damage pattern of the specimens under loading of the CAI test. Shear failure occurred along the planes, and Fig. 5-13 presents a bar chart of the shear failure angles. The angle is defined as θ (Fig. 5-12 (a)). With respect to loading direction, the angles were 45° for V-CFRP, 24° for TR-CFRP, and 16° for R-CFRP. The mechanism about why this occurred could be explained use Fig. 5-14. In Fig. 5-14, solid line represent delamination, broken line represent compression fracture line. In the case of V-CFRP, it was a typical compression fracture with 45° shear angle. In the case of TR-CFRP, no delamination zone is similar to V-CFRP. When fracture reached delamination zone, fracture went along with delamination. So the shear angle reduced to 24° due to the delamination. In the case of R-CFRP, no delamination zone is also similar to V-CFRP. Because the delamination zone is wider than that of TR-CFRP, so shear angle reduced to 16° further. Reduction of the angle was due to fiber-resin adhesion, and this was improved by surface cleaning supported by larger angles of shear failure and CAI strength.

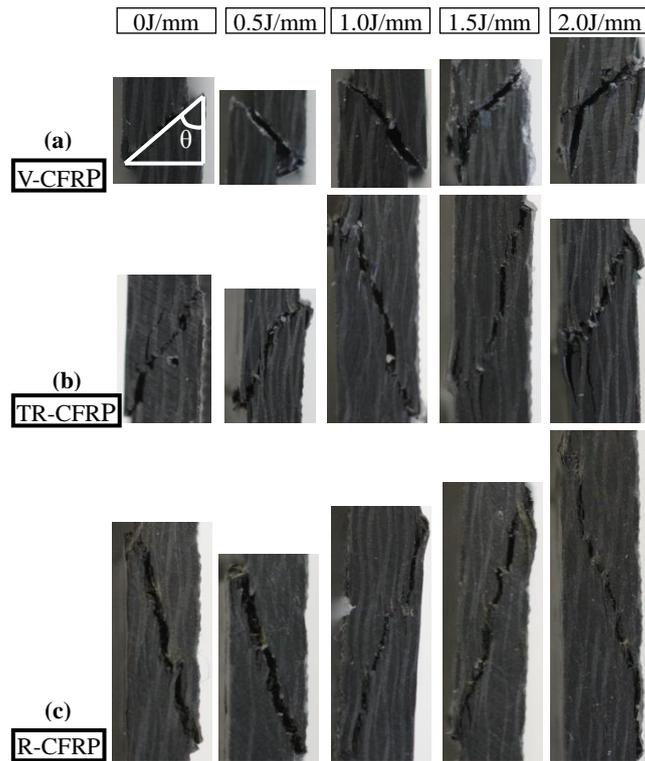


Fig. 5-12 Profile side damage pattern of the specimens. (a) V-CFRP. (b) TR-CFRP. (c) R-CFRP

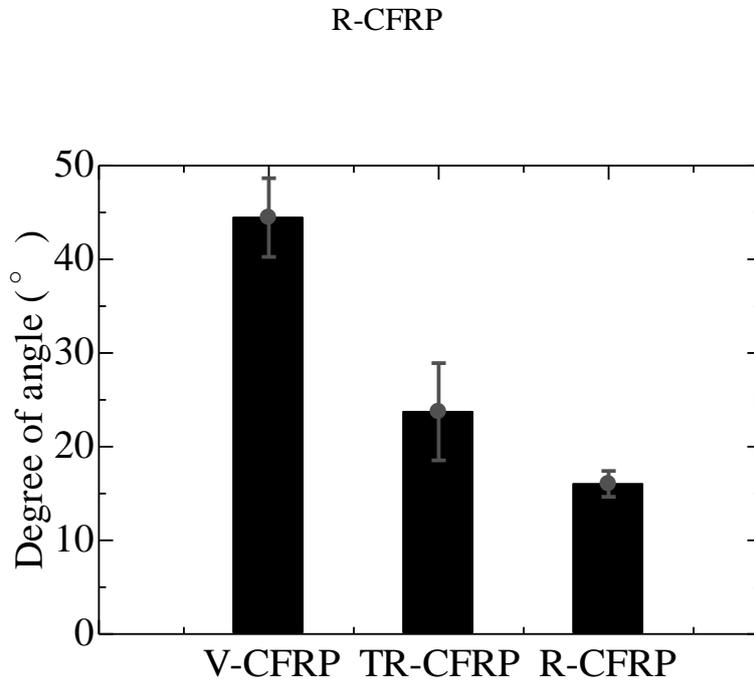


Fig. 5-13 Shear failure angles of specimens

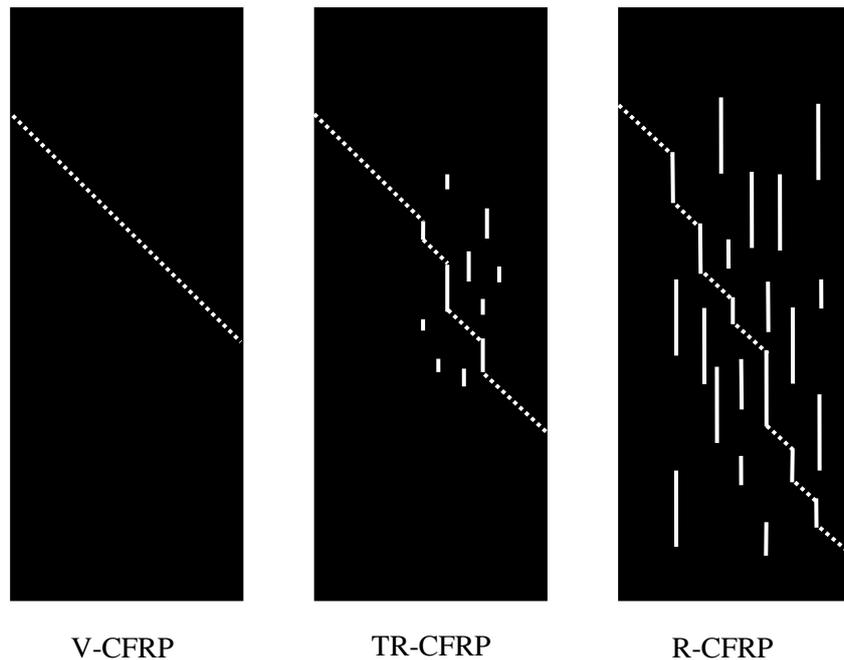


Fig. 5-14 Schematic view of shear angle

Figure 5-15 depicts sections of damaged samples impacted at an energy level of 2J/mm. The suspension for smooth grinding on the cross-section surface effectively highlights the cracks in the SEM images. Each sub-picture consists of four images: an image of the whole cross-section for marking damage location, an enlarged view of the whole cross-section image near the impact site, an enlarged view of a damage crack, and an enlarged view at fiber-visible level for adhesion analysis.

Normally, impact damage is initiated as a matrix crack, which extends to the interface of two laminates and progresses as delamination. Matrix cracks initiate as either tensile or shear cracks. In both cases, cracks are initiated transverse to the fibers within a ply. They propagate through the thickness when they come across stiffer fibers in the ply, leading to the development of delamination. The extent of delamination depends on the portion of impact energy available to fracture the interface [29].

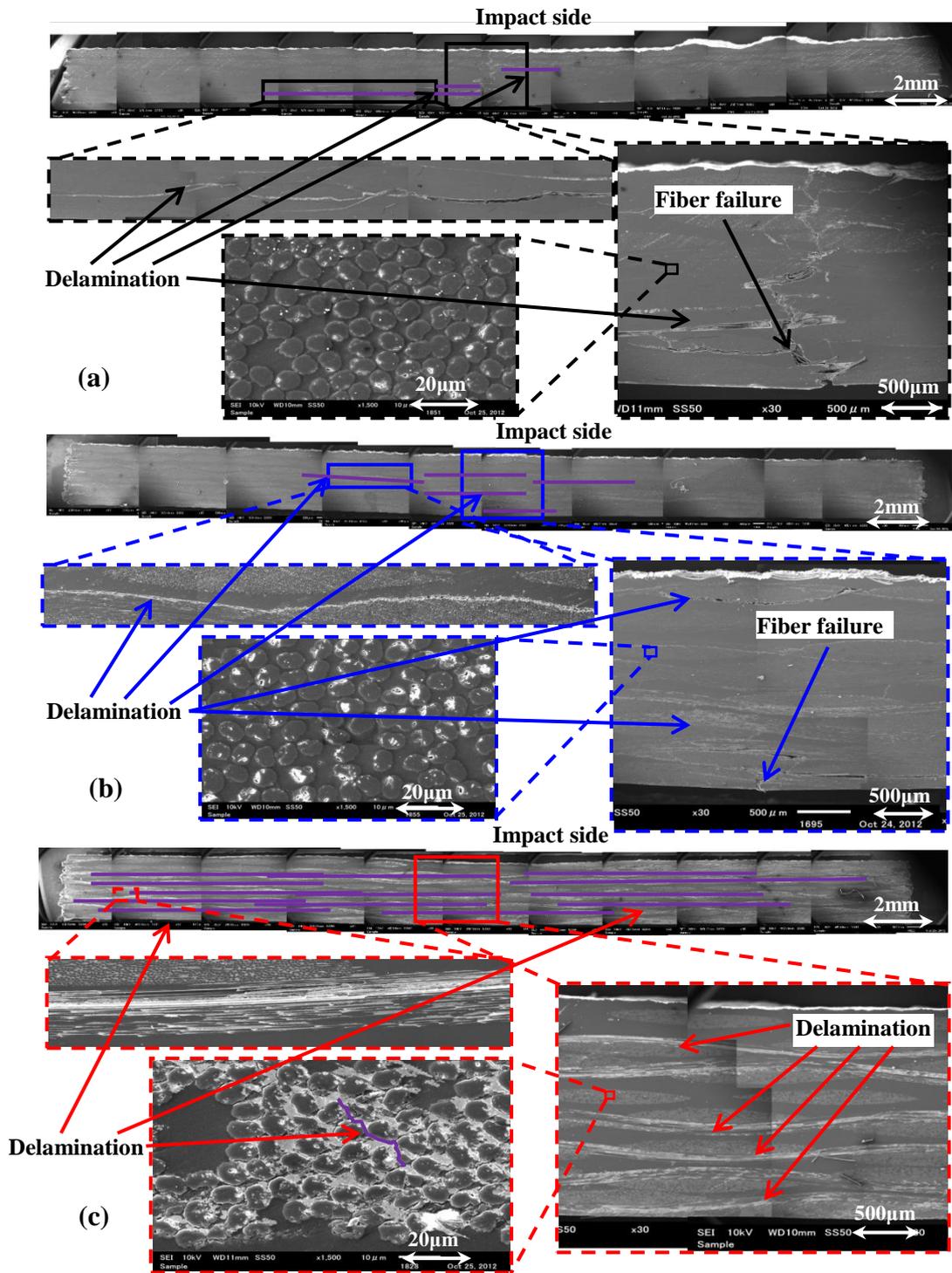


Fig. 5-15 SEM images near the impact site. All specimens impacted at the impact energy level of 2J/mm. (a) V-CFRP. (b) TR-CFRP. (c) R-CFRP

In Fig. 5-15 (a), some delamination occurred around the impact site. Fiber failure was observed on the back side of the laminate, and the damage propagated through the thickness of the laminate. For the V-CFRP, fibers run in both directions and are woven such that the fiber tows in each direction run above and below the tows in the other direction. When V-CFRP is subjected to impact loading beyond the threshold energy level, a crack is initiated within the ply. When it tries to propagate through the thickness, it has to cut through the fiber in the fill or warp direction. Unless the available energy is high enough to fracture the fiber tow, crack growth is arrested by the woven structure. Hence, delamination initiation and progression are suppressed, and delamination damage is reduced. Therefore, only a little delamination occurred. In Fig. 5-15 (c), a large amount of delamination occurred although no fiber failure was observed. When R-CFRP is subjected to impact loading beyond the threshold energy level, impact energy was absorbed and transformed to delamination for weak interlaminar adhesion which supported by published reports[16, 17]. Delamination increased and occurred around the impact site (Fig. 5-15 (b)). Fiber failure was also observed on the back side of the laminate, but was not as intense as that of V-CFRP. The results fall between V-CFRP and R-CFRP, due to previous surface cleaning. These results are strongly supported by enlarged views at the fiber-visible level in Fig. 5-15 (a), (b), and (c). The above observations are similar to the analysis results presented in sections 5.3.2 and 5.3.3.

5.4 Summary

The strong connection among recycling, remanufacturing, and the final performance of recyclates clearly affects the types of market in which recycled CFs can be introduced. For the most valuable pattern of reusing high-performance recycled CFs as CFRP, it is crucial to clarify the impact response and CAI properties of TR-CFRP and R-CFRP.

In this study, a Charpy impact procedure was used to produce low-velocity impact damage on three types of CFRP composite laminate in order to investigate the influence of recycling on impact damage resistance. The post-impact properties were studied as a measure of damage tolerance of the composite using CAI testing. From the results, the following conclusions can be drawn.

The major damage produced by impact differs for different composite laminates, due to the fiber surface state: fiber failure for V-CFRP, fiber failure and some delamination for TR-CFRP, and delamination for R-CFRP. Damage resistance is improved up to 80% of V-CFRP by surface cleaning while R-CFRP is 50% of V-CFRP.

For the most cost-effective use of limited resources, many techniques have been developed for recycling fiber-reinforced polymer. Now it is necessary to focus on using recycled CF. The results of this study will provide the basis for future applications of recycled carbon in many fields.

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CHAPTER SIX

Conclusions

Chapter 6 Conclusions

One of the most important objectives of this study is to investigate the effect of pyrolysis time and temperature on the mechanical properties of recycled fiber, based on tensile strength measurements, determining the optimum decomposition conditions for GFRP and CFRP by superheated steam. In chapter 2, the recycling of GFRP by pyrolysis was investigated in superheated steam for times ranging from 30 to 300 min at 340, 370, and 450°C. The recycling of CFRPs by pyrolysis was investigated in superheated steam for times ranging from 15 to 90min at 340°C, 390°C, and 440°C. Experiments performed in superheated steam provided resin removal efficiencies above 80wt%. Some char residue from the polymer remaining on the fibers may limit reuse options or require further processing for removal. The results of virgin fibers heated in different atmospheres indicate that high temperature and small quantity of oxygen are the main factors affecting the tensile strength of recycled fibers. Therefore, setting the temperature of pyrolysis as low as possible to obtain high-value recycled fibers is significant. Glass fibers of good mechanical quality were recovered from GFRP by using superheated steam. The tensile strength of the fibers was 3 to 5% lower than that of the virgin fibers under the optimal condition. The tensile strength of carbon fibers is near that of virgin fibers under optimal conditions, and this result is promising. The optimal pyrolysis conditions for GFRP and CFRP were determined. In this research, the optimal condition of GFRP was 370 °C and 30min, the optimal condition of CFRP was 340 °C and 30min. Under optimal condition, strength of recycled fiber dropped slightly. The reason why strength of fiber recycled under optimal pyrolysis conditions didn't reduce could be attributed to the resin which wrapped up the fiber that protected from

high temperature and small quantity of oxygen.

In chapter 3, it is possible to recycle plastic using designed plastic recycling subsystem device. From the results of FT-IR, it is confirm that plastic degraded during pyrolysis recycling process. From the results of calorific values and energy production, it is confirm that recycled pyrolysis oil could be used as a fuel in the further. The reduction of the intensity of the (–C–O–C–) stretching vibration band of the ester functional group and aromatic deformation revealed that degradation occurred. Molecular weight of recycled pyrolysis oil is lower than raw of them. It turned out that recycled pyrolysis epoxy oil contained about 30.2 kJ g⁻¹ calories and recycled pyrolysis unsaturated polyester oil contained about 36.3 kJ g⁻¹. While heavy oil contained about 40 kJ g⁻¹ calories. It is possible to use recycled pyrolysis oil as a fuel.

In chapter 4, R-GFs were treated with detergent and acetone, and R-CFs were treated with acetone and NMP. The bending strengths of FRP reinforced with treated recycled fibers were evaluated, and the effect of solutions on surface treatment and bending strength was determined. The following conclusions can be drawn from the present investigations. (1) It is possible to recycle reinforced fibers from FRP, and to remanufacture them into high-value R-FRP for reuse. (2) Acetone effectively removes unsaturated polyester resin impurities, with no adverse effect on the bending strength of TV-GFRP. The bending strength of R-GFRP could be dramatically improved (from 26% to 94%) through treatment with acetone. NMP effectively removes epoxy resin impurities, with no adverse effect on the bending strength of TV-CFRP. The bending strength of R-CFRP could be significantly improved (from 49% to 78%) through treatment with NMP. The price of reinforced fiber, especially CFs, is very high. If reinforced fiber can be recycled and remanufactured into TR-FRP with as high a

performance as possible, the value of TR-FRP will be greater than the recycling cost, and the recycling of FRP can be carried out continuously without assistance from government. These results increase the probability that this method will be widely used in the future.

In chapter 5, the strong connection among recycling, remanufacturing, and the final performance of recyclates clearly affects the types of market in which recycled CFs can be introduced. For the most valuable pattern of reusing high-performance recycled CFs as CFRP, it is crucial to clarify the impact response and CAI properties of TR-CFRP and R-CFRP. In this study, a Charpy impact procedure was used to produce low-velocity impact damage on three types of CFRP composite laminate in order to investigate the influence of recycling on impact damage resistance. The post-impact properties were studied as a measure of damage tolerance of the composite using CAI testing. From the results, the following conclusions can be drawn. The major damage produced by impact differs for different composite laminates, due to the fiber surface state: fiber failure for V-CFRP, fiber failure and some delamination for TR-CFRP, and delamination for R-CFRP. Damage resistance is improved up to 80% of V-CFRP by surface cleaning while R-CFRP is 50% of V-CFRP. For the most cost-effective use of limited resources, many techniques have been developed for recycling fiber-reinforced polymer. Now it is necessary to focus on using recycled CF. The results of this study will provide the basis for future applications of recycled carbon in many fields.

List of Publications

1. Jian SHI, and Limin BAO. Optimum decomposition conditions for glass fiber reinforced plastic recycling by superheated steam. Japan Journal of Applied Physics 2011; **50**(1): 01AJ01
2. 鮑力民、赤羽賢一、施建、劍持潔. 光ファイバセンサによる FRP エロージョンの予知. 日本複合材料学会誌 2011;**37**(6):209-215
3. Jian Shi, Limin Bao, Ryohei Kobayashi, Jun Kato and Kiyoshi Kemmochi. Reusing recycled fibers in high-value fiber-reinforced polymer composites: Improving recycled fiber-reinforced polymer bending strength by surface cleaning. Composites Science and Technology 2012; **72**(11):1298-1303
4. Shi Jian, BAO Limin, Kemmochi Kiyoshi. Low-Velocity Impact Response and Compression after Impact Assessment of Recycled Carbon Fiber-Reinforced Polymer Composites for Future Applications. Polymer Composites. (published online DOI: 10.1002/pc.22803)

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