DEVELOPMENTS IN THE FLUIDISED BED PROCESS FOR FIBRE RECOVERY FROM THERMOSET COMPOSITES

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ABSTRACT

Carbon fibre reinforced plastic (CFRP) is being used in increasing quantities particularly in the transport industry to reduce carbon emissions through weight reduction and in the energy industries for renewable technologies, such as wind turbines. As a high value and energy intensive material to manufacture a good case can be made for recovering and reusing carbon fibre from waste material. A number of companies in Europe and the USA are now in the early stages of commercial operation, but the focus is upon the recycling of clean, uncontaminated scrap from manufacturing processes and it is recognised that CFRP that is mixed with other materials eg. sandwich panels, metal inserts, painted surfaces and composites made from toughened polymers are more difficult to recycle effectively with existing commercial processes.

The fluidised bed process developed at the University of Nottingham for recovering carbon fibre from waste composite material has the potential to process mixed and contaminated CFRP waste. The oxidising conditions allow full removal of any organic materials and the fluidised bed effectively separates the carbon fibres from other incombustible materials, such as metals. The process has now been developed to a scale representative of commercial operation and a waste CFRP comprising intermediate modulus carbon fibre and toughened epoxy resin has been processed successfully and good quality recycled fibres recovered. This paper will present the results and discuss the quality of the carbon fibre recovered from the process. A discussion of some of the key requirements to build a viable fluidised bed plant will also be presented.

1 INTRODUCTION

1.1 Background

Increasingly carbon fibre recycling process development is transitioning from lab scale to commercial scale plant. A number of recycling operations are running successfully worldwide with major operations in the USA, UK, Japan and Germany. There are still some major challenges to overcome to develop a genuine use-re-use cycle, for instance; maintaining product quality and consistency across a wide range of waste CFRP material types and formats and high levels of hand labour typically associated with preparation of materials for recycling. In addition, the lack of established markets into which to sell recovered fibre is a significant barrier, this is fundamentally due to the significant change in material form from virgin materials (continuous tow) to recovered fibre, which is in a discontinuous, filamentised form with low bulk density.

A key question for future progress is the value of the recovered fibres. The intrinsic value of carbon fibres is due to their high cost as virgin materials but excessive levels of touch labour associated with recovery and potentially high levels of energy use to a great extent weaken the business case for recycling activities.

2 RECYCLING PROCESS DEVELOPMENT

2.1 Process requirements

Commercial recovery processes are currently targeting throughput levels of around 1,000 tons per annum. This provides a reasonable match for current production levels of waste CFRP (currently dominated by scrap tow and dry fabric) but future scale-up of planned aerospace programmes and the potential widespread use of carbon fibre in automotive applications means there will be much higher levels of end of life composites in the future.

Candidate fibre recovery processes must exhibit consistent performance across a wide range of material types (predominantly epoxy resins) and cope with e.g. changes in thickness of laminates. Low energy and labour levels are primary requirements. Waste CFRP from manufacturing processes may be in a relatively clean form but end-of-life materials and some forms of manufacturing waste may have significant levels of contamination from, for instance, metal inserts, metallic or polymer honeycomb or foam cores (sandwich panels) and other polymers/paints. Fibres should retain high mechanical properties and preferably be in a physical form which is easily converted into a valuable product. Typical conversion routes are milling to sub-mm fibre lengths, pelletisation for injection moulding compounds and non-woven mat manufacture. Whilst existing commercial fibre recovery processes are well suited to relatively clean, uniform waste materials, other more mixed and contaminated waste is more difficult.

2.2 The Fluidised Bed process

A fluidised bed process for the recovery of carbon fibres has been under development at The University of Nottingham since the turn of the century [1, 2], initially at a laboratory scale and more recently at a scale representative of a commercial operation.

The polymer is removed from the scrap composite in a bed of silica sand fluidized by air operating at a temperature in excess of 500 °C. The oxidizing atmosphere means that the pyrolytic char formed by thermal decomposition of the polymer matrix is oxidized leaving clean fibres. These fibres are elutriated from the fluidised bed, carried out in the gas stream and subsequently separated from the gas stream in a cyclone (Figure 1).

The gas stream is then heated to high temperature to fully oxidize any remaining volatiles gases and energy recovery takes place to preheat incoming air. As the process combines air classification with fibre recovery, it has been shown to be particularly robust in dealing with end-of-life components that may contain mixtures of different material and other contaminants. Organic material is oxidized and separated from the fibres and any metallic material remains in the fluidized bed from where it can be removed in a continuous or batch sand regrading process.

The process is inherently suited to comminuted materials with a mean fibre length under 25mm. the process therefore requires low labour levels throughout. The drawbacks of the fluidized bed process are the requirement for large volumes of high temperature air and the reduction of fibre properties through mechanical action in the bubbling sand bed.

2.3 Process flow

A commercial process is significantly more complex that a lab scale process and additionally involves several other process steps that must be demonstrated to a high technology readiness level (TRL). Figure 2 shows some of the critical process steps with emphasis placed on preparation of composites for recovery.

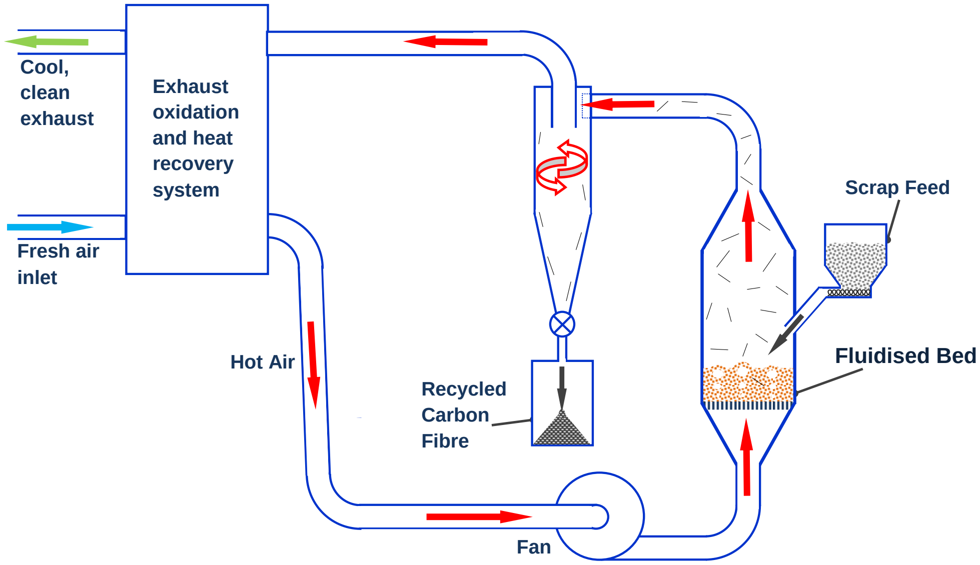

Figure 1 Fluidised bed process schematic

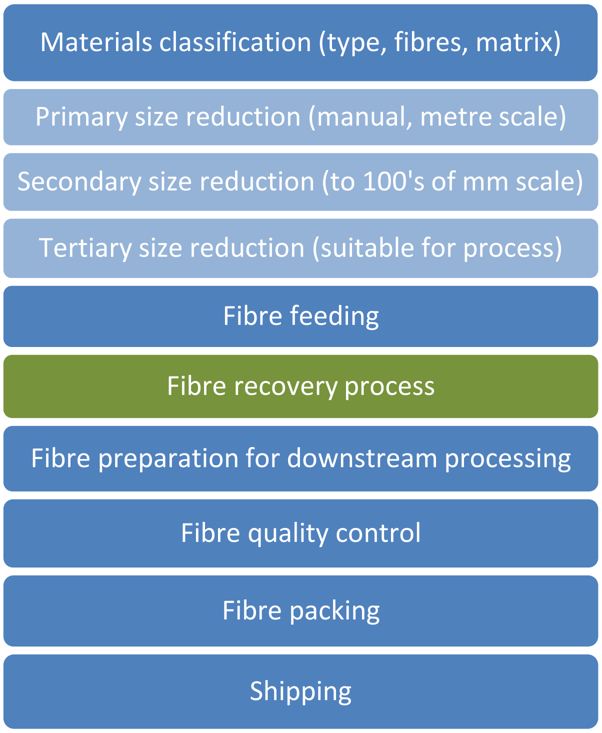

Figure 2 Typical fibre recovery process flow

2.4 Fibre recovery process

A photograph of the pilot process plant recently commissioned is shown in Figure 3, it is of a scale representative of commercial operation. The plant also includes exhaust gas treatment and heat recovery (not shown). Composite preparation and packing activities take place in the enclosed area shown towards the left of the image. The plant is capable of processing materials from a wide range of sources. These are shredded first in a slow speed primary reduction process and this is followed by a hammer mill to produce CFRP fragments graded to the requirements of the fluidised bed. The fibres in the input feed should be less than 25mm. However, shorter fibres can be processed with a greater throughput rate and the mean fibre length in the feed would therefore depend on the application for the recovered fibre. The shredded CFRP can be fed continuously into the fluidised through a metered feeding system and an air lock. The fluidised bed operates at a pressure slightly below atmospheric pressure to ensure that no gases from the process leak into the environment. The recovered fibre is removed continuously from the bottom of the cyclone and can be packed directly into bags. Any residual contamination remaining in the fluidised bed can be removed by an air operated sand regrading system.

The exhaust gases leaving the cyclone still have some residual organic content as the temperature in the fluidised bed is insufficient for complete oxidation of the polymer. They are therefore fed into a high temperature oxidiser which is also equipped with a high efficiency heat recovery system to minimise the gas fuel input required, during continuous operation. The cool, clean exhaust gases pass to atmosphere. Careful choice heat exchangers and system design is needed to provide the high levels of heat recovery required for a viable operation. High levels of insulation are also recommended on the high temperature pipework to minimise heat losses. As the process operates below atmospheric pressure the pipework, fan and valves should also minimise in leakage of air as this also increases the energy requirement of the process. Whilst the processing of waste CFRP made with halogenated resins would require a more sophisticated pollution control system, this is not required for the vast majority of waste CFRP available.

The fluidised bed process is intended to operate continuously and at steady state. Since there is a substantial thermal mass in the fluidised bed and the high temperature pipework, heating up and cooling sown on a daily basis would significantly increase the energy consumption of the process. The energy input to bring the process up to operating temperature is provided by the gas burner in the high temperature oxidiser, which can fire at high level during warm up, reducing, once the bed is up to temperature.

Figure 3 Pilot scale Fluidised Bed plant

3 RESULTS

3.1 Fibre preparation process

The current process utilises a two-stage size reduction – large structure would first need to be reduced in size to metre-sized pieces that could then be fed into a twin shaft shredder to reduce the size of the pieces to around 25-100mm scale. Thereafter, the waste is fed to a hammer mill with a screen size appropriate for the process. Table 1 shows a summary of data; energy usage levels are dependent on the final size required.

Table 1 Size reduction processes

Shredding process	Scale	Method	Energy use
Secondary size reduction	25-100mm	Twin shaft shredder	0.04 MJ/kg
Tertiary size reduction	5-25mm	Hammer Mill	0.22 MJ/kg

The following images show the form of the composite after secondary and tertiary size reduction processes.

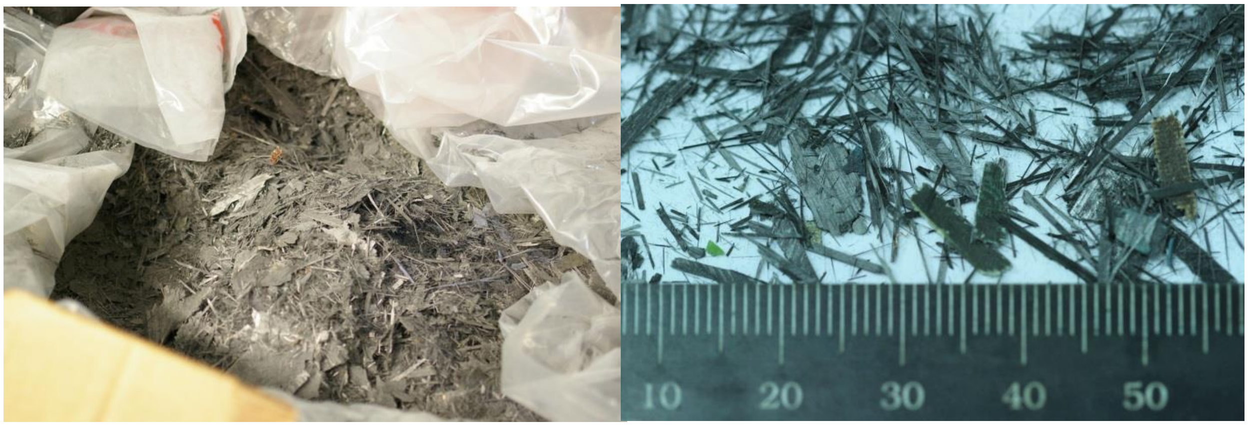

Figure 4 Left: Shredded carbon/epoxy prepreg laminate (secondary size reduction), Right: Composite ready for feeding to the fluisdised bed

3.2 Energy use

A thermal model of the fluidised bed process has been developed to consider the energy requirements for a commercially operating plant. The pilot plant has been designed to provide operational flexibility to allow for process development and the pipework system is more complex and longer in length than would be required in practice. The thermal model can be used to simulate plants of various annual throughput with a variable feed rate per unit area of fluidised bed. The following assumptions have been used:

- Optimised levels of insulation on high temperature pipework.
- Optimised plant configuration to minimise pipework length but allow for practical operation and maintenance.
- Minimal air in leakage in sub-atmospheric pipework.
- High efficiency heat recovery system using regenerative heat exchanger technology.
- Continuous plant operation.

The modelling has considered a plant sized for continuous operation with an annual output of recovered carbon fibre in the range 50 to 800 tonnes. The feedrate of carbon fibre in the waste is varied from 5 to 20 kg/hr per square metre of fluidised bed area. The results are shown in Figure 5 and the energy requirement includes both gas for the oxidiser and electricity for the fans and other ancillaries. A significant result is that the annual throughput of the plant does not have a major influence on energy requirement, but the most important parameter is the feed rate of waste per unit area of the fluidised bed. Virgin carbon fibre has an energy requirement for manufacture typically well in excess of 300 MJ/kg [4, 5]. It can be seen that the energy required to recover the carbon fibre is less than 10% of the energy to make virgin fibre and an energy input of less than 5% would be achievable provided that higher feed rates per square metre of bed are employed.

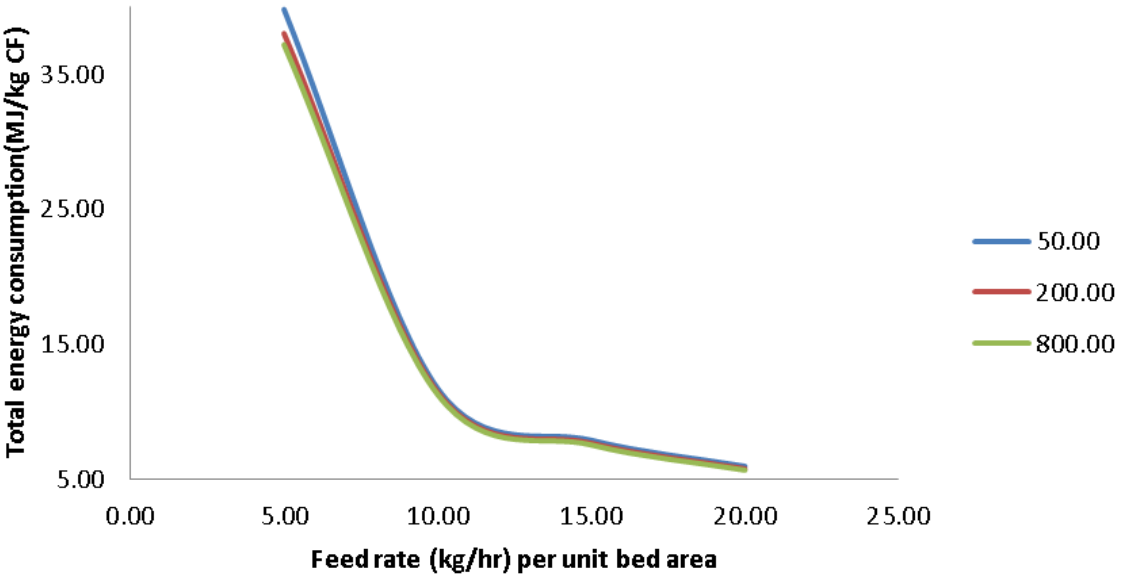

Figure 5 Total (fuel + electrical) energy required to operate a fluidised bed process at annual outputs of 50, 200 and 800 tonnes of recovered carbon fibre.

3.3 Fibre properties

In some processes it may be possible to recover long carbon fibres but most processes suitable for end of life materials will deliver short discontinuous fibres which are challenging both to reuse and to test. The fluidised bed process produces a recyclate with a fluffy form, as shown in Figure 6 in which the carbon fibre is in the form of individual filaments with a distribution of fibre length. A clean fibre recyclate is produced with no substantial residue on the surface.

A waste CFRP with Toray T800 carbon fibre and a toughened epoxy matrix has been processed and the carbon fibres recovered and tested for mechanical property retention. The mechanical properties of the recovered fibres are generally good. Measurements of stiffness show that the recycling process generally yielded fibres with a stiffness similar to that of virgin fibre.

Single fibre tensile testing was carried out according to BS/ISO 11566. Fibres were tested at a 4mm gauge length on a Tinus Olsen Hounsfield load frame using a 5N load cell at a rate of 1mm/min. Fibres were mounted on paper card and positioned in the loading frame so that the fibre axis and machine load axis were concurrent. Additional testing was carried out at 3mm and 5mm gauge length under the same conditions for purposes of determining compliance as per Annex A of BS/ISO 11566. Virgin T800S carbon fibre was tested using the same procedures but using Dia-Stron's LEX 820/ LDS 0200 integrated test platform. 15 fibres recycled using the fludised bed were also run through the Dia-Stron system so fibre diameter could be measured. The diameter of the recycled fibres was measured to be 4.91µm and the diameter of virgin fibres was the same within experimental limits measuring 4.93 µm. Weibull median ranks were used to calculate the shape and scale parameters for both sets of fibres. The scale parameter for virgin fibres was 6,507MPa while the recycled fibres showed a loss in strength of less than 20% having a scale parameter of 5,331MPa. The shape parameter was very similar for both fibres: 5.17 for the virgin and 4.99 for the recycled. The graphs below show the mean tensile strength and elastic modulus of the virgin and recycled fibres. The error bars represent standard deviation.

Figure 6 Recycled fibre raw form showing fluffy, discontinuous, 3D random & highly entangled structure

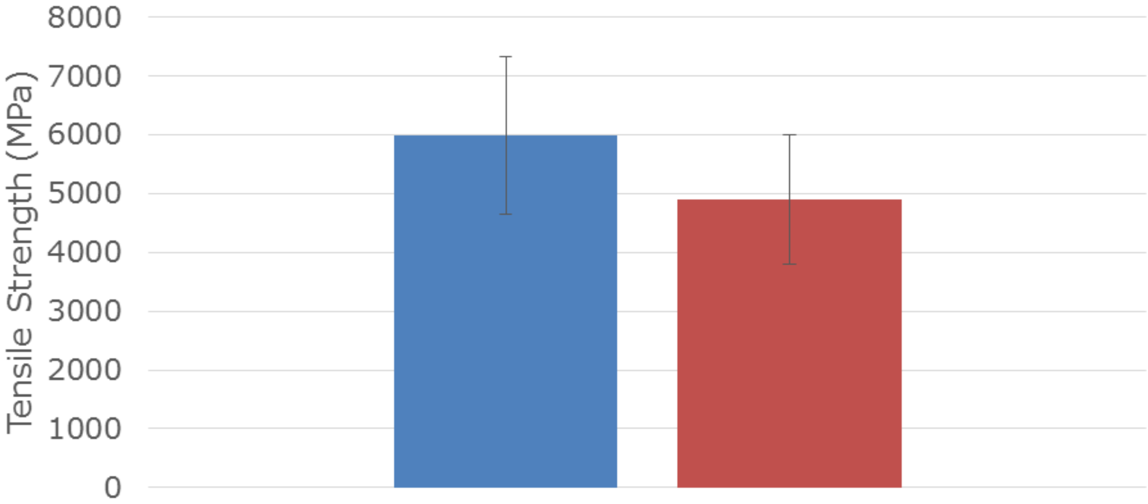

Figure 7. Tensile Strength (virgin T800 fibres in blue, recovered fibres in red)

The mean tensile strength and the Weibull scale parameters show strong agreement. Tensile strength of the recycled fibres is 4,896MPa, 18.2% lower than the 5,986MPa tensile strength of the virgin fibres. There was a small increase in stiffness of the recycled fibres over that of the virgin fibres but it is well within the standard deviation and not considered a significant increase. Virgin T800s fibres were determined to have an elastic modulus of 308GPa and the recycled fibres were 334GPa.

Previous results for carbon fibres recovered using a smaller scale laboratory fluidized bed have shown similar modulus to virgin carbon fibre, but reductions in strength ranging from 25 to 50%

[3]. The strength reduction of 18% reported here for the pilot scale plant is therefore better than has previously been reported for a fluidised bed process and is an encouraging result. Whilst commercial pyrolysis processes can be optimized to give reductions in carbon fibre strength 5% to 10%, these processes are not able to process the variety of mixed and contaminated waste that the fluidised bed can.

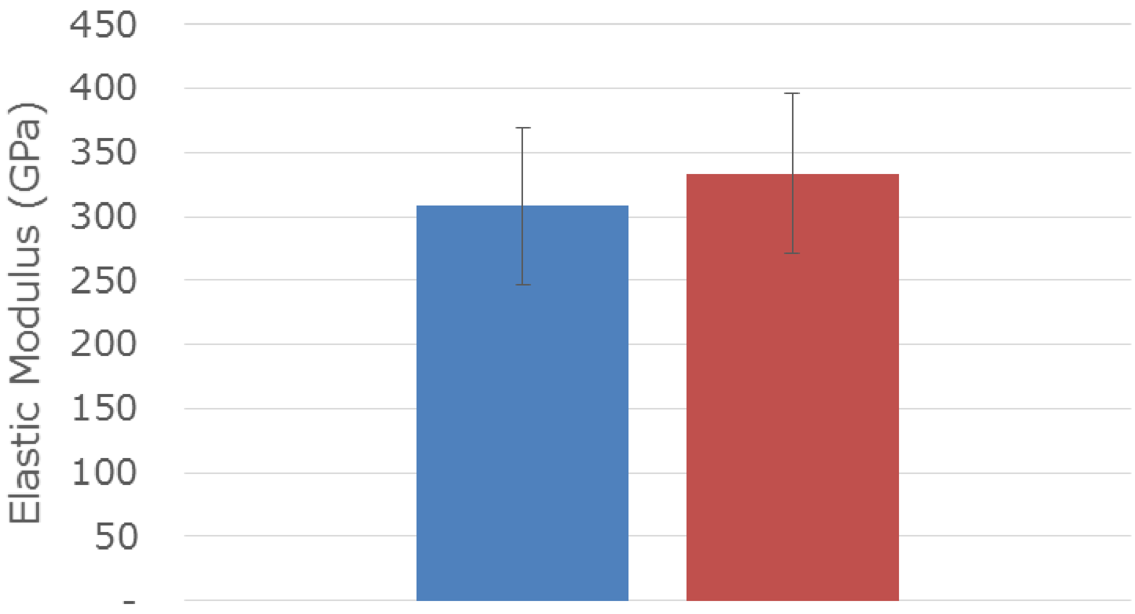

Figure 8 Elastic Modulus (virgin T800 fibres in blue, recovered fibres in red)

4 CONCLUSIONS

A fluidised bed process for the recovery of carbon fibre from waste CFRP has been scaled up to a pilot plant representative of a commercial scale operation. The process is particularly suitable for the treatment of mixed and contaminated CFRP waste. Initial results from the processing of a composite comprising Toray T800 carbon fibre and a toughened epoxy resin show that good quality carbon fibre can be recovered with no significant reduction in tensile modulus and a reduction in tensile strength of 18%, which is less than has been previously reported for any carbon fibre recovered using a fluidised bed. An energy analysis of a fluidised bed process designed for commercial operation has shown that the total energy input required to recover the carbon fibre is typically 5-10% of that needed to manufacture virgin carbon fibre.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

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