RECYCLING OF CARBON FIBRE COMPOSITES

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INTRODUCTION

Carbon fibre reinforced composite materials have enormous potential in the transport and wind energy sectors because of their durability, light weight and ability to be manufactured in complex shapes. However, most composites use thermosetting resin matrices, which are not easily recycled. Thermoset polymers cannot be melted down and remoulded like thermoplastics; as such there exist numerous technical challenges to overcome in order to commercially recycle composite materials.

There are several factors that underpin the significance of the composite recycling industry moving forward. Firstly, the legislative drivers, such as the Waste Landfill Directive [1]. More industry specific legislation such as the End of Life Vehicle Directive (ELV) [2] and Waste Electrical and Electronic Equipment (WEEE) [3] indicate the need for an efficient method of recycling, as opposed to landfill disposal. Landfill disposal is the least desirable end of life option, while (formerly) the most cost effective, it is the least resource efficient [4]. The ELV is particularly important since it places the burden of recycling on part manufacturers, which means that end of life options (such as composite recycling) should be considered while designing new vehicles.

Carbon fibres are valuable and their production is very energy intensive. Another factor supporting carbon fibre composite recycling relates to the projected market size of composites and the subsequent waste estimates. Figure 1 demonstrates a graph of mass in kilotonnes vs year, the bars represent composite demand for various industries, and the black dots represent composite waste. By considering various estimates of lifespan in different industries, as well as production ramp rates, an estimate for waste can be determined. If the data in Figure 1 is representative of future estimates, then there will be an associated increase in waste that lags behind demand depending on the lifespan of the products in each industry. The aforementioned legislative drivers behind carbon fibre recycling were undoubtedly based on an estimation of similar nature to Figure 1, across a number of different material markets.

This study will describe the technical and economic challenges associated with the recycling of carbon fibres, the state of the art in recycling technologies and the re-use of fibres in high performance composites.

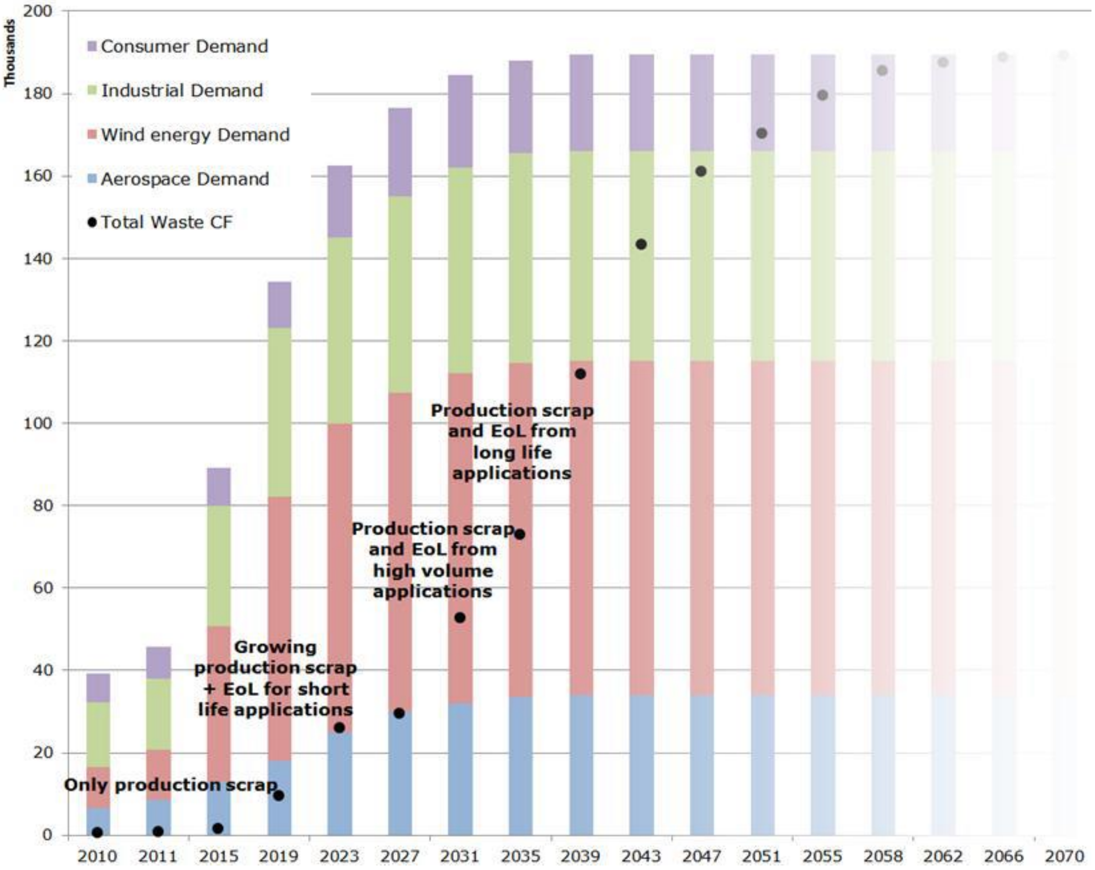

Figure 1. Graph of composite demand (bars) and waste (dots) in kilotonnes by year [5].

COMPOSITES RECYCLING

A number of different methods have been developed (with varying levels of maturity) to recycle composite materials in novel ways.

The three main types of composite recycling are mechanical, thermal and chemical methods [4]. Composite recycling processes can alternatively be divided into primary, secondary and tertiary processes [6]. Primary and secondary processes are typically mechanical recycling, indicating various stages of scrap size reduction, such as large scale size reduction, followed by a second size reduction process. Tertiary processes cover thermal and chemical processes, due to the way in which these processes recover more than just fibres, whether it is energy recovery and/or the recovery of organic components [6, 7].

Currently there are 6 commercialised composite recycling operations, 3 of which recycle carbon fibre composite [8]. ELG Carbon Fibre in the UK uses a pyrolysis process and recycles dry carbon fibre waste, prepreg waste and laminates; they produce 2000 tonnes/year of recovered fibre, products include chopped/milled/pelletized fibre, random mats and discontinuous fibre yarns. CFK Valley Stade Recycling GmbH recycles all forms of carbon fibre waste using a pyrolysis process, and outputs 1000 tonnes/year, products include milled fibre, pellets and electromagnetic interference shielding. Materials Innovation Technologies (MIT) in the USA recycles all types of carbon fibre waste into nonwoven rolled goods, chopped fibre for compounding and long fibre reinforced thermoplastic applications, at a capacity of 2000 tonnes/year.

1. Mechanical recycling

Mechanical recycling processes are typically one or a number of size reduction methods applied to composite scrap. Large scrap pieces are size reduced by slow speed crushing, typically a crushing mill, or large granulator [4]. A secondary size reduction stage then takes place using a high speed hammer mill or shredder. Following this, the material can be graded by sieving or via a cyclone. Typical sizes of recyclate produced are as large as 10mm, and as small as 50 m or smaller. The lower end of the size spectrum is essentially powder, and can be used as fillers in other composites to varying degrees of success [4].

Palmer et al (2009) showed a successful closed loop mechanical recycling process by mechanically recycling composite and using it as filler in a dough moulding compound (DMC) process [9]. The results showed between 92-97% flexural strength and <90% flexural modulus compared to DMC without the recyclate [9], an acceptable drop in mechanical properties in many applications. Re-using mechanical recyclate reduces costs associated with virgin materials. However the mechanical recyclate absorbs more resin than standard calcium carbonate filler, which leads the moulding compound to be more viscous, which in turn could increase manufacturing costs [10]. However it is necessary to observe that mixing virgin and recycled fibres and obtaining 50% of the mechanical properties suggests this process is not viable [10].

The shortcomings of mechanical recycling however are generally the lack of a market, coupled with the low value of the recyclate produced. In the past this has caused a number of companies to fold due to market saturation of low quality recyclate. There are a number of LCAs (Life Cycle Analyses) that are attempting to demonstrate the environmental benefits of mechanical recycling. One recent paper has done just that, and yielded a result of 2 MJ/kg by using a milling process at 10kg/hr, and 0.27MJ/kg at a rate of 150kg/hr [11]. This work is important because it lends validation to a large scale recycling operation, if composite scrap were to be prepared in a centralized plant for example.

2. Chemical recycling

Chemical recycling processes employ chemical compounds, catalysts or solvents as a predominant part of the process. Chemical methods include traditional solvent solutions, whereby the solvent reacts with the composite resin and removes it. Some studies use a solution of peroxide hydrogen and dimethylformamide showed tensile strength retention of 97% compared to virgin fibres [12]. However the process took 30 minutes, which is characteristic of chemical processes, the reaction time is not quick. In addition to this, there are concerns about the use of large amounts of hazardous solvents, which can create complex, costly waste scenarios.

Most research into chemical recycling methods is aimed at supercritical fluids. A fluid is supercritical when exposed to a particular temperature and pressure, above which conventional material phases no longer apply, allowing behaviours such as effusing through solids like a gas, and dissolving materials like a liquid. Supercritical water can be used as a low cost and environmentally agreeable recycling media [13] Supercritical methods employing the use of a catalyst have also been studied [14]. Supercritical methods have gained favour through use of environmentally friendly recycling media, however they are currently limited to lab scale only, there are a number of scale up challenges to be addressed.

3. Thermal recycling

Thermal recycling methods include pyrolysis and fluidised bed processes. The main difference between primary and secondary (mechanical), and tertiary (thermal and chemical) processes is the recovery of individual fibres. The carbon fibres are the most valuable part of the composite, so it follows that should these fibres be recovered, the value of the recycled product exceeds that produced solely by mechanical methods [4]. In addition to this, thermal recycling methods have a greater likelihood to achieve closed loop recycling, which entails recovering individual fibres, but also harnessing the reaction energy in some useful way.

Pyrolysis processes recycle material in an atmosphere free of oxygen, often nitrogen. Without oxygen, combustible material breaks down into lower molecular weight components, and leaves char on the surface of the composite. There is a pyrolysis stage of resin degradation in air, but by removing oxygen, the degradation can only reach a certain stage [4]. The hydrocarbon products can be used as fuels to add heat to the process, since the reaction is exothermic [4]. However since pyrolysis processes by themselves leave char on the surface of the composite, individual fibres cannot be liberated by a single process step, therefore an oxidation step is required to remove the char and recover the fibres.

Adherent Technologies, Inc. has developed a catalytic pyrolysis process. The pyrolysis process is performed at a relatively low temperature of 200 C, and with the aid of a catalyst, individual carbon fibres are freed from resin [4, 15].The tensile strength of the recovered fibres was found to be between 1 and 17% less than virgin fibres. Recycled Carbon Fibre Ltd employs a belt pyrolysis process to recycle carbon fibre [16]. The process consists of two large reactors; in the first stage temperature is tightly controlled as the resin degrades. In the second stage, a stream of air consisting of fumes from the first stage mixed with oxygen, in order to remove the char [16]. However most belt pyrolysis processes are limited to very specific forms of recyclate, in terms of thickness and resin composition. This is due to temperature homogeneity through the whole thickness of a part, variable thickness parts could need additional cycles to completely recycle. The temperature and belt speed have to be calibrated for individual compositions, therefore a mixture of different wastes could mean that the recycling is not homogeneous.

Fluidised bed recycling has been pursued by the University of Nottingham for around 20 years. Originally the process was designed to recycle glass fibre, but early work suggested that despite the significantly greater market share of glass fibre over carbon fibre, the loss in tensile strength was too great, and the value of the recyclate was too low [4]. The fluidised bed process consists of a bed of silica sand with average particle diameter less than 1 mm. The sand is fluidised by a stream of hot air passing through a distributor plate, at a superficial velocity in excess of 0.4 m/s at a temperature typically above 500 C. The resin burns off the composite and the char degrades, when sufficient char has degraded, individual fibres break off and are elutriated along with the gases released from the resin. Following elutriation, the fibres are separated from the gas stream by a cyclone separator and deposited into a collection bin. The gas stream enters a secondary high temperature combustion process in order to oxidize them.

One key aspect of the fluidised bed process is the inclusion of all necessary process steps in a single processing step (apart from size reduction), composite scrap goes in, and fluffy fibres come out. Currently granulation is the process used to prepare composite scrap for fluidised bed processing, however the effects on the recycled fibres between different comminution processes is not well understood [17].

An additional benefit is that the fluidised bed has a very high tolerance for waste contamination [17]. The manufacturing scrap has a lot of rivets, bolts and other fittings occasionally found within pieces of scrap (see Figure 2). The fluidised bed will simply collect these fittings in the bed, while the composite around them is recycled. Of course if too much contamination of this nature builds up, fluidisation quality will be affected. Fibres typically show a 20% reduction in tensile strength, and roughly 10% drop in stiffness [4].

Figure 2. Contaminated composite scrap.

FLUIDISED BED AT PILOT SCALE. SCALE-UP CHALLENGES

Scaling up a fluidised bed process is a significant step in making the process commercially viable. Currently the carbon fibre recycling industry faces two main challenges:

- Development of a cost effective, high throughput process.
- Production of valuable recyclate with good retention of properties.

A pilot scale fluidised bed is available at the University of Nottingham, in order to make the transition into a fully commercial process (Figure 3). However, before commercialization, some key areas need to be addressed. The three main stages of a fluidised bed recycling process must be covered: preparation, processing and packing.

The preparation stage covers any process applied to material before it goes into the fluidised bed. Using a stable fluidized bed process, the effects of different forms of preparation can accurately be determined based on the yield of fibres from the process, and the time it takes to process a specific mass of feed. Preparation of material is an area tightly linked into the market for the final product. For example if the final product requires fibres of a specific length range, this can be addressed by a shredding process specific to generating composite feed of relative size.

Figure 3. Fluidised bed at pilot scale located at the University of Nottingham.

Another area of interest is tied to the thermal side of the fluidised bed process. Generating high throughput is an important factor for composite recycling since it forms a basis for the cost effectiveness of the process. Though previous work done in this area shows that throughput can have a hard cap. Wong (2006) suggested that no feed mass greater than 40g should be present in a bed of 0.312mm diameter, else the fluidisation behaviour transitions to a sub-optimal, spouting state [18]. However it is unclear how this behaviour scales with the diameter of a larger bed, and there is evidence to suggest that this behaviour is highly fibre length dependent.

Previous work in the group has also shown how important process temperature is on residence time and fibre property retention [19, 20]. However Jiamjiroch (2012) has demonstrated that agglomerates can form inside a fluidised bed (Figure 4) [20]. It is currently unclear exactly how these agglomerates form, and what state the fibres that form them are in (i.e. free fibres, or bundles with partially degraded resin). Agglomerates have been an area of interest since they were observed in a fluidised bed. So it follows the key to high throughput in a fluidised bed is the intricate understanding of how fluidisation affects, and is affected by feed distribution in the bed, and the process temperature that provides the most efficient rate of fibre elutriation.

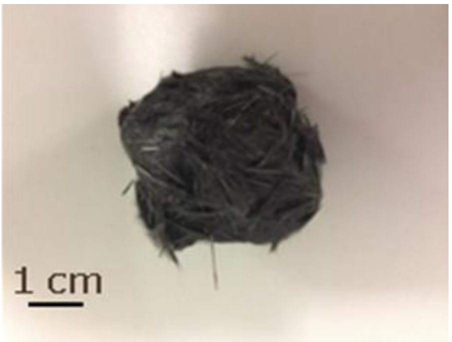

Figure 4. A series of agglomerated recovered from a fluidised bed

The recycled carbon fibres are in a fluffy form comprising individual fibre filaments (Figure 5). The fibres are clean and show very little surface contamination. Carbon fibres show a lower strength degradation (< 20 %) with retention of the original stiffness. Fibres do not show any measurable oxidation.

Figure 5. Recycled carbon fibres (fluidised bed).

Another important challenge for the economically viable up-scaling is related to the packing system of the recycled fibres. The packing stage is any process that occurs after the fibres leave the cyclone from the processing stage. An effective way of taking fibres from a collection bin and packaging them is an aspect of the process that is highly desirable on a commercial level, since it removes labour costs. The packing stage of the process will be geared around the fibre product itself and how to organize it after processing.

Energy requirements across a fluidised bed process cover all these key areas, the preparation and processing of the composite, as well as the packaging of the final recycled product. As the process scales up to handle more material and generate higher throughput per year, novel ways of managing energy are required to keep costs down. It is essential for the success of a carbon fibre recycling process that carbon fibres are recovered at much reduced energy levels than virgin fibres (< 10 %). Otherwise the incineration with energy recovery would be more favourable.

RE-USE CHALLENGES

The value of the recycled fibres is dependent on the fibre properties, if recycled fibres can retain high strength and modulus, they can be re-used in lieu of virgin fibres, which is a cost reduction from every angle. Low value recyclate, such as that obtained from primary recycling methods has limited usability due to the means in which it is produced. The product loses most of its tensile strength and fibre length [4]. The better the retention of properties of recycled fibres, the more varied the reusable market can be. A broad market in itself is the apex for recycled fibres, and that market already exists if the recycled fibres can retain adequate properties to meet it.

Regarding the re-use of recycled fibres, it is currently unclear what form of recyclate will generate the most lucrative market. Previous attempts by ERCOM and others suggest that milled fibre is not this market [4]. Nevertheless, the whole process can be optimized for a specific recyclate form.

A very specific shredding process can be developed to prepare the feed. This then has implications on the optimum process parameters for the whole process.

Improved mechanical properties can be achieved when fibres are aligned in a composite, thus several research projects are investigating / have investigated production methods to cost-effectively align the short recycled fibres [21]. At present the authors are not aware of any commercially available products incorporating aligned recycled fibre, though some technologies may be close to market.

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