Electron Beam Assisted Recycling of Carbon-Fiber-Reinforced Plastics

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ABSTRACT

Upward trends in carbon-fiber-reinforced plastic (CFRP) consumption are discussed. Commercial aerospace industry relies heavily on CFRP with the design of new jets from Airbus and Boeing using over 50% CFRP. The auto industry is using CFRP at a growing rate, with some experts suggesting that production CFRP cars are in the near future. Sporting equipment has also seen a large increase in the use of CFRP over the past few years. When these items reach the end of their useful life, can they be recycled? Advantages and disadvantages of chemical extraction, fluidized bed, pyrolysis, and radiation-related methods are assessed. Electron beam irradiation-assisted recycling of CFRP and the possibility of producing low-cost chopped carbon-fibers are discussed.

KEYWORDS
Electron Beam, Carbon Fiber Recycling

1. INTRODUCTION

Gravitational forces dictate the fuel efficiencies of aircraft, automobiles, motorcycles, and bicycles; therefore, low-weight properties are an important feature for materials used in their construction. High-strength properties are needed to withstand high-impact objects in the path of transportation vehicles and aircraft. In aircraft, high strength properties are also required to withstand pressure from the high velocity cruising speeds, which result in large internal stresses on the structural components of the aircraft. Lightweight, high-strength materials are also important features in the manufacturing components of sporting goods such as hockey sticks and lacrosse sticks. The use of carbon-fiber-reinforced plastic (CFRP) in the design of applications like those mentioned is growing because there is a large demand for strong composite materials that require small amounts of energy to move. CFRP fulfills these structural demands.
1.1. CFRP Market Growth

According to a report produced by an association of composite companies and research institutes (CCeV), global demand for CFRP, which has doubled since 2008, is expected to increase from 48,000 tonnes to 130,000 tonnes in 2020 (1). The leading industry in consumption of CFRP is the wind turbine industry, which currently uses 23% of total global consumption (1). This is in part due to the overall increasing size of turbines. Modern turbines are over 100 times the size of those constructed in 1980 (2).

The aerospace and defense industries contribute a healthy 18% to CFRP consumption (1). High fuel prices, rising passenger expectations, and increasing environmental concerns are causing airlines to demand more from manufacturers (3). As a result, new designs for the jumbo plane models (Boeing 787 Dreamliner and Airbus A350XWB) use more than 50% CRFP in their construction (3). Sports and leisure followed by molding and compounds consume the third and fourth most amounts of CFRP globally (1).

With respect to CFRP, the automotive industry will be another market to observe. Rolls Royce, Aston Martin and Porsche are using CFRP for various parts such as bonnets, front wings, door openings, trunk enclosures and lids, along with both front and rear bumper assemblies (4). Automobile manufacturers find the design and styling flexibility of carbon-fiber particularly attractive along with the enhancement of an automobile’s power-to-weight ratio (4). Manufacturers are able to replace traditional steel and aluminum with CFRP, while experiencing no loss in strength or stiffness (4).

1.2. Recycling

This large CFRP growth estimate will inevitably lead to larger amounts of waste material. While 40% of pre-preg CFRP is waste from trims and rips during fabrication (5), careful attention should be paid to the increases in CFRP material that has and will be nearing the end of its in-service life cycle. Wind turbines have a 20-25 year lifecycle and it is predicted by 2034, that around 250,000 tonnes of rotor blade material will need to be recycled annually (2). With the commercial jet manufacturing industry producing CFRP-heavy planes, the amount of recyclable material will substantially increase over the next decade. Boeing expects 8,500 commercial planes to be retired by 2025 (6).

Currently, many retired commercial jets end up in desert scrap yards (6). European legislation has already put heavy restrictions on dumping reinforced plastics into landfills, and European automobile manufacturers will be required to use 85% recyclable material in new vehicles after 2015 (7). Legislation by the United States and other large consumers could follow suit due to the potential energy savings. According to research published by Boeing (6), the energy usage and materials cost to manufacture virgin carbon-fiber is 25-75 kWh/lb and $15-30/lb, respectively. The energy usage and materials cost to manufacture recycled carbon-fiber is 1.3-4.5 kWh/lb and $8-12/lb, respectively (6). That is approximately 70% of the cost and less than 5% of the electricity to manufacture recycled carbon-fiber in comparison to virgin carbon-fiber. The same study claims that if 2 million pounds of carbon-fiber scrap, which is the expected 2014 quantity produced by commercial jet manufacturing, were to be recycled, it would save enough electricity to power 175,000 homes per year (6).

2. Current Recycling Methods

Mechanical recycling breaks down CFRPs into smaller pieces so that they can be reused as filler in other composite materials (7). The carbon-fibers are not actually “reclaimed” and because the focus of future work by at SUNY-ESF is on a method involving fiber recovery, the subject of mechanical recycling of CFRPs will not be discussed further. Methods that reclaim carbon-fibers, such as chemical extraction,
fluidized bed, pyrolysis and radiation assisted methods will be described. As these methods are described, it should be noted that there are three primary goals when recycling CFRPs: 1. the removal of the resin from the fibers, 2. the capture of the resin byproducts, 3. the retention of the mechanical properties of the fibers (5).

2.1. Chemical Extraction

The resins used in CFRP are typically thermosets such as epoxies and vinyl esters, which dissolve over time in strong solvents. A few excellent reviews exist that compare different fiber reclamation processes (8, 7, 9). A catalytic tertiary process was implemented at a pilot plant in the United States over ten years ago, with short-term processing capabilities able to reach 1,000 tonnes per year (7). Another pilot plant in Japan uses a system that incorporates a benzyl-alcohol with a catalyst in a nitrogen atmosphere to dissolve epoxy resins (7).

Supercritical fluids are very dense, viscous fluids in the supercritical phase with excellent diffusion and dissolving power (7). Researchers at Nottingham University showed that water and short-chain alcohols (most notably propanol) have proved successful in quickly dissolving epoxy resins (5, 11); however, experimentation is in a laboratory setting. Larger scale, continuous processes may be a difficult challenge to overcome (9).

While chemical methods of recycling CFRP produce reclaimed fibers with high retention of mechanical properties and fiber length, the methods have flaws as well. One example is that using powerful solvents has detrimental environmental effects. Another downside is that most of these methods are going to be difficult to implement at a commercial scale (9), and lastly, adhesion of the reclaimed carbon-fiber to polymeric resins is commonly reduced by chemical recycling methods (7).

2.2. Fluidized Bed

Researchers at University of Nottingham also developed the fluidized bed method of recycling for carbon-fiber composites (12). The method uses a bed of silica sand, which is fluidized with an oxygen-rich stream of air at temperatures of about 550°C (8). The polymer volatilizes and the stream carries fibers away. The process is continuous with a high contamination tolerance, but there is no chance at resin recovery (8, 7). However, by installing a secondary combustion chamber for resins, energy recovery is a possibility (8). Reclaimed fibers are unstructured with at least a 20% loss of stiffness (8), but there is very little residual char left on them (7) and high potential for surface bonding (8).

2.3. Pyrolysis

Pyrolysis of CFRPs is a method that heats the material in an inert atmosphere, limiting oxidation, and therefore reducing thermal damage to carbon-fibers (8, 7). This process has been extensively studied with most results producing a high-quality carbon-fiber and low molecular weight hydrocarbons as recovered byproducts from the resins (8).

The pyrolysis method can result in hazardous off gassing and some residual char may be left on the fibers, nevertheless, the process is solvent-free (7). Temperatures used in pyrolysis range from 450-700°C, with the higher end needed to avoid char formation on the fibers. High-strength fibers and resin byproduct recovery are the factors attributing to the construction of pyrolysis plants in the US, UK, Japan, Germany and Italy (7). Currently used by Boeing, pyrolysis has become the world’s most established recycling process for CFRP (7, 9).
2.4. Radiation Related Methods

Experimentation with radiation-enhanced recycling methods is still in the early stages. Milled Carbon Ltd attempted a method using radio frequency heating, however the material is required to be metal-free (13), which is a difficult requirement when recycling CFRP. Researchers at University of Nottingham experimented with a microwave heating system. The process was determined to be feasible, with fiber tensile strength values slightly better than results obtained from a fluidized bed study, and a small, 12% reduction in tensile modulus (14).

New experimentation with a combined chemical and electron beam (EB) process was conducted in Poland by Nowicki et al. (15). The epoxy resins were swelled to 30% hydrogen peroxide content and irradiated with an electron beam. At 200 kGy, there was a 71% drop in bending strength. At 1,000 kGy, there was an 86% drop. The degradation appeared to taper off as the dose level reached levels this high, and it was stated that the majority of hydrogen peroxide had been consumed in reactions up to that point. The resins were not, however, completely dissolved.

The aromatic ring structure of epoxy and vinyl ester resins results in radiation resistant properties. Nowicki et al. (15) also attributes the low oxygen diffusion coefficient to radiation resistance as well. Longieras et al. (16) found that at doses as high as 1 MGy, decomposition was negligible, and therefore any successful process will require the use of a co-treatment (15).

3. CFRP Work at SUNY ESF

SUNY ESF is currently working on an innovative, hybrid, EB-assisted pyrolysis process to recycle CFRCs that has not been tried before. Milled Carbon Ltd. in England has a well-established recycling plant, running a pyrolysis oven with a 900°C capability, which normally runs at 600°C (13). Our goal is to use electron beam radiation to lower the pyrolysis temperature by 200-400°C. Irradiation is being conducted at IBA Industrial, located in Edgewood, NY, using their 3 MeV, 250 kW Dynamitron EB. The carbon-fibers produced will be a low-cost alternative to expensive, energy-intensive carbon-fibers that are currently used for sporting goods, decorative and non-structural composite products.

After cooling, the samples will be analyzed for percent degradation of the resin, char on the fibers, and fiber strength using ASTM D4018, and then compared with fiber strength before pyrolysis. Carbon-fibers are not degraded by electron beam; they have actually been shown to significantly increase in tensile strength at a 300 kGy dose level (17). We believe that this new process will produce better byproduct control. The degraded byproducts, collected in the cold trap, will be analyzed by gas chromatography/mass spectrometry to determine the major components.

4. Conclusion

As previously discussed, other methods of fiber-reclamation exist, however, each has advantages and disadvantages. Chemical methods show excellent results at the laboratory scale, but show little promise in developing a system at the commercial scale (15, 7). The fluid bed method has potential, but so far is producing low quality fibers and has limited byproduct recovery capability (8, 7). Lastly, conventional pyrolysis requires extreme temperatures to ensure char-free fibers. Electron beam assisted pyrolysis would improve CFRP reclamation in the three crucial areas: efficient removal of resin from fibers, more predictable capture of resin byproducts and good retention of, if not improved fiber mechanical properties.

Along with these improvements, it is hoped that added energy savings and environmental benefits will result from the use of the hybrid, EB-assisted pyrolysis process. The ultimate goal is to bring the energy...
required to produce carbon-fiber from 1.3-4.5 kWh/lb. to 0.7-2.5 kWh/lb. If the EB-assisted pyrolysis could also be made faster than conventional pyrolysis, fewer or smaller recycling facilities would be needed, improving land usage.

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