



Conversion of the matrix in glass fiber reinforced composites into a high heating value oil and other valuable feedstocks



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ABSTRACT

Waste from glass fiber reinforced polymer composites has become an imminent problem worldwide. Emerging recycling technologies, such as chemical recycling, have shown to be promising for economically viable recovery of high-value carbon fibers. Similar interest for recovery of glass fibers is negligible due to their low value. In this study, a solvolytical conversion of the polyester matrix from glass fiber reinforced composites was proposed, to increase the cost effectivity for the recycling of these materials. Simultaneously with the recovery of glass fibers, an oil product was produced. The produced oil could be used as a potentially valuable fuel with heating values up to 39.6 MJ/kg, or a petrochemical feedstock for production of chemicals and materials. Using this technology, an environmental problem can be eliminated by converting the waste into valuable products.

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1. Introduction

Fiber reinforced polymer (FRP) composites have become essential materials in a range of engineering applications. The major application sectors are transportation, construction, and building constructions [1]. The global production of composite materials was estimated to exceed >10 million tons in 2015, which at the end-of-life will occupy >5 million cubic meters [2]. Glass fiber reinforced polymer (GFRP) composites are the dominant reinforcing material accounting for >90% of all the FRP's currently produced [2]. Approx. 60% of this volume accounts for GFRP composites with thermosetting polymers as the matrix. Wind energy is one of the areas where GFRP thermoset polymers are widely used, and with accelerating growth in the sector, it has been predicted that 6 million tons GFRP blade material will be produced globally over the coming decade [3]. With a lifetime of 10–25 years for a wind turbine, efficient recycling routes are urgently needed.

Currently, most FRP composites end up in landfills or are being incinerated at the end of the life cycle, because recycling is difficult due to the complex composition (fibers, matrix and fillers) and the crosslinked nature of the thermosetting polymer. However, landfilling does not solve the waste problems, as the materials are not biodegradable.

Incineration of the plastic wastes and recovering energy is related to unacceptable emissions of gasses such as nitrous- and sulphur oxides, dust and dioxins [4]. Furthermore, the heating values of FRP composites are relatively low due to the content of fibers (30–70 vol.% [5]) and mineral fillers in the composites, why incineration is not a sustainable disposal route for composite waste.

In order to protect the environment, and reduce the amount of organic materials that are being landfilled, the European Union implemented several directives, the Waste Framework Directive, which was amended in 1991 (Directive 91/689/EC), the Landfill Directive in 1999 (Directive 99/31/EC) and the end-of-life vehicle directive in 2000 (Directive 2000/53/EC) to promote sustainable solutions for FRP waste. These directives resulted in the prohibition to landfill composite waste in some EU countries [6]. As a consequence of legislation, the development of more advanced recycling technologies was required. Recycling technologies such as thermal recycling [7–9], mechanical recycling [10–12] and chemical recycling are among the most studied methodologies.

According to a review paper by Morin et al. [13], chemical recycling using near- and supercritical fluids has shown to be the most promising recycling technology, because the carbon fibers can be recovered clean and with mechanical properties similar to the virgin carbon fibers. Furthermore, the undamaged carbon fibers can be obtained at relatively low temperatures and by the use of relative environmental friendly solvents, such as water, acetone, ethanol, propanol, methanol etc. to break down the polymer matrix [14–21]. The benefits of recovering carbon fibers using chemical solvolysis are also supported by the studies conducted by Princaud et al. [22]. They showed that it is more environmentally sustainable to recover the carbon fibers by hydrolysis, than

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landfilling the carbon fiber reinforced polymer (CFRP) composites. In fact, they found that the recovery of carbon fibers by hydrolysis results in an average gain of approx. 80% for all eco-indicators, when compared to landfilling.

The potential of using recycled carbon fibers in second generation composites to close the loop on the CFRP composite life-cycle has been reviewed by Pimenta et al. [23]. Their work shows that it is possible to manufacture composites from recycled carbon fibers, such as a car door panel, an aircraft seat arm rest, Corvette wheelhouse etc. However, they concluded that the re-manufacturing process is problematic, especially with regard to retaining the necessary mechanical properties of the composites.

Recovery of clean glass fibers has also been achieved using chemical recycling. However, the mechanical properties of the glass fibers are decreased significantly compared to the recovered carbon fibers [14–15]. Decreased mechanical properties of the recovered glass fibers together with their low value compared to carbon fibers, makes chemical recycling of GFRP's a challenge.

The sustainability of GFRP recycling can be increased by conversion of the polymer into valuable products, as presented by Cunliffe et al. [24]. They produced a liquid fuel oil from a polyester/styrene copolymer by pyrolysis at 450 °C using a fixed bed reactor. A range of other researchers have also performed thermal degradation of polymers to produce fuel oil at temperatures >400 °C [25–29].

The aim of this study was to use low temperature (200–325 °C) solvolysis in the presence of acetone for production of liquid fuel oil from the polymer matrix of GFR composites. The goal was to determine if the sustainability of GFRP composite recycling could be increased by innovative application of chemical solvolysis for recovery of glass fibers combined with conversion of the resin into a high heating value oil, and thereby closing the loop on the GFRP/CFRP life cycle. Acetone has previously shown to be efficient for solvolysing the polymer matrix of GFRP composites at temperatures 260–300 °C [16–18]. Acetone can also be considered as a non-toxic solvent, which is a favorable property when selecting solvents. However, the application of acetone as solvent can also be related with high process costs. Therefore, in order to reduce the solvent costs by half and to obtain the effect of mixing solvents, a mix of water and acetone 50/50 vol.% together with the catalyst KOH, was used in this study. Furthermore, the present acetone-water-KOH system has not been used before according to literatures to degrade composites, thus providing important developments in the chemical recycling field.

The composition of the oil was characterized by GC-MS, element analysis, metal content analysis and ash content. Physical properties of the oil were characterized by density measurements, viscosity measurements, higher heating value (HHV) analysis and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Composite materials and chemicals

The composite materials used in this study were GFR unsaturated polyester (UP) resin. The UP resin was made from maleic anhydride, phthalic anhydride and propylene glycol, which were cross-linked with styrene. Since the composites were manufactured by industrial partners, information about the precise weight percent of each monomer cannot be provided. The composite specimens used for the solvolysis experiments ranged in sizes from 50 × 20 × 10 mm to 100 × 40 × 10 mm. The resin content of the composite, evaluated by calcination following the recommendation of the standard DS/EN ISO 1172, was 27.2 wt.% ± 0.2 based on the average of the value measured on three samples.

Table 1 shows the elemental composition, metal content and higher heating value (HHV) of the composite used in this study, see Section 2.3 for methodology. Prior to the analyses, approx. 1 g of the composite

Table 1
Characteristics of the polymer composite waste.

Analysis of composite	
Ultimate analysis (%wt.)	
Carbon	42.7
Hydrogen	4.9
Nitrogen	2.9
Oxygen	<0.1
Sulphur	0.4
Metal analysis (mg/g composite)	
Aluminium	4.0
Boron	0.44
Copper	<0.1
Iron	1.96
Potassium	0.3
Phosphor	0.03
Zinc	<0.1
Strontium	0.05
Calcium	9.8
Cadmium	<0.1
Cobalt	<0.1
Chromium	<0.1
Vanadium	<0.1
Proximate analysis	
Higher heating value (MJ/kg)	7.9
Density (g/mL)	1.17
Fiber content (%wt.)	72.85
Resin content (%wt.)	27.15

specimen was crushed into a uniform mix of glass fibers, fillers and matrix. The chemical analyses were performed directly on this mix, without any further separation. The composite had a HHV of 7.9 MJ/kg and contained smaller amounts of elements such as Al, B, Fe and Ca, which have been a part of the glass fibers and filler material in the composites [30]. Acetone (ACS reagent grade with a purity of 99.5%) and hexane (Chromasolv for HPLC with a purity of ≥97.0%) were purchased from Aldrich Denmark and potassium hydroxide (KOH) pellets (ACS analyse grade ≥ 85.0%) were purchased from Merck Germany. The water applied was distilled water.

2.2. High temperature solvolysis procedure

Degradation of the composite specimens was performed in a non-stirred 280-mL high pressure batch reactor constructed in 316 stainless steel (BC-1, HIP - High Pressure Equipment, USA) with an electrical heating mantle and internal Pt-100 temperature measurement device. The composite specimens were placed in the reactor together with the solvent and catalysts. The reactor was then sealed and heated to the desired conversion temperature at a heating rate of 5 °C/min. Pressure was induced by the increasing temperature, the amount of the composite and the volume of the solvent. Samples were treated for 30 min at the conversion temperature after which the heating mantle was removed to allow the reactor to cool. The reactor was opened after cooling to approx. 50 °C by natural convection with a duration time of approx. 2 h. The recovered fibers were collected from the reactor and washed with portions of acetone until the acetone became clear and then with demineralized water to remove residue KOH from the surface of the fibers. After washing, the fibers were dried in an oven at 80 °C for 24 h and their weights were used to calculate the percentage degraded resin by Eq. 1.

$$\text{Degradedresin (\%)} = \left(\frac{\text{Weightofcomposite} - \text{weightofsolidresidue}}{\text{Weightofresinincomposite}} \right) \cdot 100 \quad (1)$$

To determine the effect of temperature and catalyst on the resin degradation efficiency and oil yield, the recycling process was carried out using the series of experiments listed in Table 2. The experiments were performed using the solvent mixture 50/50 vol.% acetone/water

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