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Optimized process for recovery of glass- and carbon fibers with retained mechanical properties by means of near- and supercritical fluids

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ABSTRACT

Degradation of hybrid fiber composites using near-critical water or supercritical acetone has been investigated in this study. Process parameters such as temperature (T = 260–300 °C), pressure (p = 60–300 bar) and composite/solvent (c/s = 0.29–2.1 g/mL) ratio were varied to determine the effect on the resin degradation efficiency and the quality of the recovered glass and carbon fibers. Supercritical acetone at 260 °C, 60 bar and a c/s ratio up to 2.1 g/mL could achieve nearly complete degradation of the resin. The glass fibers were recovered with up to 89% retained tensile strength compared to the virgin glass fibers. The use of near-critical water reduced the tensile strength of the glass fibers by up to 65%, whereas the carbon fibers were recovered with retained tensile strength compared to the virgin carbon fibers using water or acetone.

1. Introduction

Fiber reinforced polymer composites are a type of material with increasingly more engineering applications due to their high strength to weight ratios, low cost and corrosion resistance etc. They are used in different engineering applications such as aerospace, constructions and offshore applications [1]. According to the Composite Market Report from 2015, the global production of composite materials exceeded 8.8 million tonnes in 2014. Glass fiber reinforcement is the dominant reinforcing material with more than 90% of all the fiber reinforced composites currently produced. Approx. 60% of this volume accounts for composites with thermosetting polymers as the matrix. The remaining 10% of the global production of composite materials accounts for carbon-and aramid fiber reinforced composites, where the global carbon fiber reinforced polymer demand was estimated to 92.000 tonnes in 2015 [2].

The major disadvantage of these materials is the lack of recycling. They are not biodegradable and cannot be melted and remolded into new materials [3]. Therefore, as the production of composites increases, so will the volumes of end of life waste too [2]. Despite the fact that waste management has been of high priority in the European Union (EU) in the last decades, most of the composite waste is still landfilled [4,5].

Landfilling is not a sustainable solution in the long term and several European directives has resulted in stricter regulations in several EU countries, including prohibition to landfill composite in Sweden and Germany [6]. Since the beginning of the 1980s, many efforts have been made to develop recycling solutions for fiber reinforced polymer composites. The recycling technologies are generally divided into three categories: Mechanical recycling, thermal recycling and chemical recycling [4,6].

Chemical recycling, also called solvolysis, refers to processes using a solvent to separate the fibers from the matrix material. Solvents can be water or organic solvents such as acetone, ethanol or propanol. The solvent is brought to high pressure and temperature to break down the polymer matrix [7,8]. The main advantage of solvolysis is the possibility to recover both the matrix material and the fibers from composites. Several studies have investigated the de-polymerization process and demonstrated successful recovery of the monomers and other degradation products from the polymer matrix [9–16]. The sustainability of chemical recycling can be increased by the possibility to reuse the solvent in a closed loop in the process. Sokoli et al. [10] showed that the acetone used for the solvolysis process could be distilled and re-used.

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Table 1
Review of studies conducted on chemical degradation of glass or carbon fiber reinforced polymer composites.

Fiber	Solvent	T (°C)	p (bar)	Reaction time (min)	c/s ratio (g/mL)	Efficiency (wt. %)	TS loss (%)	Reference
Carbon	Water	400	270	30	0.167	79	2–10	Hernanz et al. [18]
Carbon	Ethanol	450	80	15.5	0.167	79	1–16	Hernanz et al. [18]
Carbon	Propanol	450	250	40	0.1	95	1–16	Hernanz et al. [19]
Carbon	Ethylene glycol	400	–	0	–	92	0	Yildirir et al. [20]
Carbon	Ethylene glycol/water	400	–	0	–	98	3	Yildirir et al. [20]
Carbon	Water	315	90	30	0.033	95	0	Liu et al. [21]
Carbon	Water	260	–	105	0.2	100	0	Yuyan et al. [22]
Carbon	Methanol	270	80	90	–	100	9	Okajima et al. [23]
Carbon	Propanol	>450	>50	–	–	–	5	Hyde et al. [24]
Carbon	Propanol	310	52	20	–	–	0–2	Jiang et al. [25]
Carbon	Acetone	320	10	20	–	100	0	Okajima et al. [26]
Glass	Water	300	85	30	0.027	100	50	Oliveux et al. [16]
Glass	Water	275	60	120	0.21	48	35	Oliveux et al. [16]
Glass	Water	350	–	5	0.3	69	58	Kao et al. [17]

The challenges, which have prevented chemical recycling to be implemented on an industrial scale are the properties of the recovered fibers and the high consumption of solvents and energy of the process.

Regarding the properties of the recovered fibers, it has been demonstrated that carbon fibers maintain most of their tensile strength for a range of different conditions, cf. Table 1. However, glass fibers have only been recovered with significantly reduced mechanical properties compared to the virgin glass fibers [16,17]. The decrease in tensile strength of glass fibers is suggested to be due to the high temperature used and the presence of the solvent. Water has shown to be the most detrimental solvent and reduces the tensile strength of the glass fibers by 40–70%, depending on the process temperature, cf. Table 1 [16,17].

However, investigations conducted by Kamimura et al. [27] reported that the use of methanol at 275 °C, 97–126 bar and 9 h reaction time degraded 91.6% of the resin and recovered glass fibers with an average reduction of tensile strength by 7% compared to virgin glass fibers. However, a description of the tensile strength measurement methodology was not provided in the paper, making it difficult to compare the results with other investigations.

Thomason et al. [28] demonstrated strength regeneration of recycled glass fibers with reduced mechanical properties by developing a sizing on the glass fiber surface. However, an additional treatment will also increase the cost of the recycled glass fibers, which may not be competitive, compared to virgin glass fibers [8].

Regarding the solvents and energy consumption of the process, two solvolysis processes are currently available for commercial exploitation [29,30]. The techniques provide clean and high quality carbon fibers; but they also consume high amounts of solvent and energy due to the high processing temperatures or the need to use three processes in combination [8,29,30]. Thus, the solvolysis process could be optimized, to ensure a more viable recovery process.

In order to participate in the efforts of bringing chemical recycling of fiber reinforced thermoset composites from a laboratory to an industrial scale, a low temperature and pressure process using a large composite to solvent ratio is crucial. This will lead to reduced amounts of solvent and therefore reduced cost. In addition, it is necessary to understand the degradation mechanism of glass fibers and the effect of solvent during chemical recycling.

In this study, a hybrid fiber reinforced composite was solvolyzed in near-critical water and supercritical acetone at temperatures in the range of 260–300 °C, pressures in the range of 60–300 bar and composite/solvent ratios in the range of 0.24–2.1 g/mL. The effect of the process parameters and the nature of solvent on the mechanical properties of the recovered glass- and carbon fibers will be investigated. To the best of our knowledge, such high composite/solvent ratios has not been used previously in literature when recovering glass and carbon fibers (cf. Table 1), particularly not at temperatures and pressures down to 260 °C and 60 bar.

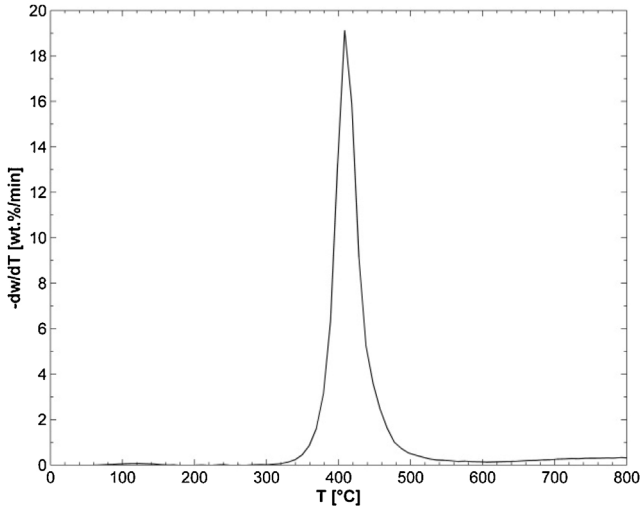

Fig. 1. TGA analysis of the pre-preg composite material.

2. Experimental methodology

2.1. Materials

A hybrid reinforced composite was manufactured at the Technical University of Denmark using vacuum assisted resin transfer moulding. This laminate was composed of E-glass and carbon fibers impregnated in an epoxy matrix (Araldite® LY 1564 SP). A one stage curing profile was used for this panel, which corresponds to a curing at room temperature for 48 h. No post cure was carried out. Thermogravimetric analyses (TGA) were performed (cf. Section 2.3.4 for methodology) on the pre-preg composite material to produce a derivative mass loss curve (Fig. 1). The cured epoxy resin is degraded in the temperature interval 360–500 °C in one weight loss peak.

The hybrid fiber composite specimens were produced in pieces of 100 mm length, 40 mm width and 9 mm thickness, where 1 cm was cut off each specimen to determine the weight content of glass fibers, carbon fibers and matrix following standard ASTM D 3171-99 extended to characterize carbon/glass hybrids, cf. Table 2 [31]. The gravimetric composition of the manufactured composite material was approx. 20 wt.% carbon fibers 52 wt.% of glass fibers. The experiments were performed on samples of 90 mm length, 40 mm

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