



Towards understanding the breakdown and mechanisms of glass fiber reinforced polyester composites in sub-critical water using some of the most employed and efficient additives from literature

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ABSTRACT

This study describes the hydrolysis of glass fiber reinforced unsaturated polyester (UP) composites using some of the most employed and efficient additives from the literature. This includes the use of KOH, a mix of KOH/phenol and reference experiments without additives. Sub-critical water in a temperature range of 200–325 °C and a constant pressure of 300 bar were chosen as process parameters to cover a wide temperature range.

It was possible to explain the mechanisms producing the majority of the different reaction products identified by GC-MS. The monomer phthalic anhydride was only recovered in the experiments without additives and was most stable at 200–250 °C. The increase or decrease in the production of monomers and other reaction products at different temperatures with and without additives has been clarified by the GC-MS investigations, which introduces new possibilities for tailoring the production of monomers and various chemical compounds via hydrolysis of polymer composites.

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1. Introduction

Fiber reinforced polymer composites (FRPC) are used in almost every type of advanced engineering structure. The major application sectors include transportation, aerospace, ships, boats and in civil infrastructure such as bridges and buildings. The usage of FRPC continues to grow at an impressive rate, which can be attributed to their advantageous characteristics, such as high strength to weight ratios, corrosion resistance, high specific strength and specific stiffness [1]. According to the Composite Market Report from 2015, the worldwide carbon fiber reinforced plastic (CRP) demand was estimated at 92.000 t in 2015 and the glass fiber reinforced polymer (GRP) demand was estimated at 1.069 mega t in 2015 only in Europe [2]. As the polymer composite industry continues to grow, production scrap and End-of-Life waste also increase at an alarming rate.

This has become a global problem, due to the low recyclability of thermoset composites. In the last few decades, the principal waste

disposal routes for composites have been landfills and incinerators. Because the polymer resin in the composite materials is not biodegradable, the economic costs of such disposal routes can be very high. Therefore, changes have been made in European legislation, which enforces more strict control of composite disposal. The development of alternative and more feasible recycling routes for composite waste is necessary. The main recycling technologies that are investigated the most includes: mechanical recycling, thermal recycling and chemical recycling [3].

Mechanical recycling involves grinding of the composite waste into smaller granulates that can be employed as fillers or partial reinforcements in new materials, such as in cement production. Mechanical recycling has been investigated by several authors [4–6]; however, it is not possible to separate the fibers from the resin using this recycling technique or recover the monomers. Thermal recycling involves chemical decomposition caused by heat. The resin is decomposed into gasses and oil, releasing the fibers and fillers. However, for GRP composites, the mechanical properties of the glass fibers are reduced considerably [7–10].

According to the review articles by Morin et al. [11] and Oliveux et al. [12], chemical recycling is the most promising alternative to depolymerize the resin and recover the glass- and carbon fibers with retained mechanical properties [13]. Chemical recycling

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enables recovery of valuable products from the resin, such as monomers and other valuable degradation products. In the investigations conducted by Sokoli et al. [14], nearly pure phthalic acid monomer from polyester resin was recovered by means of sub-critical water. In another investigation, the polymer was converted into high heating value oil with properties close to that of crude oil from the North Sea [15].

The polymer can be depolymerized with benign solvents such as water [13–25], acetone [13,15] and alcohols [26–31] at elevated temperatures and pressures. The majority of the investigations have been conducted on CRP composites (mostly with epoxy resin as the matrix) due to the higher value of carbon fibers compared to glass fibers. The interest in these investigations was mainly based on regenerating the fibers and not on the degradation products produced from the resin. However, in order to close the loop on the GRP/CRP composite life cycle, valorization of the polymer matrix is considered important too. This includes recovery of monomers or degradation products with high value for the industry.

Several authors have reported different degradation products identified after the chemical solvolysis of the polymer matrix in composites [13–34]. However, no detailed reactions mechanisms at different temperatures have been provided so far.

The objective of this research is to 1) evaluate on the reaction products produced after subjecting GFR UP composites to sub-critical water in the absence or presence of alkaline additives widely used in the field, 2) propose reaction mechanisms producing the various reaction products. Temperatures from 200 °C to 325 °C were used in this study. GC-MS techniques were used to analyze the liquid product.

2. Experimental section

2.1. Materials and methods

The composite materials used in this study were unsaturated polyester resin (UP) reinforced with glass fibers. The UP resin pre-polymer was made from maleic anhydride, phthalic anhydride and propylene glycol, which was cross-linked with styrene, cf. Fig. 1. The composite sample size was 100 mm × 40 mm × 10 mm with a weight of 75 g ± 10 g. The resin and glass fiber content was evaluated by calcination following the recommendation of the standard DS/EN ISO 1172. The resin content was 27.15 wt % ± 0.2 wt % and the glass fiber content was 72.85% ± 0.2 wt %, based on the average of the value measured on three samples. Acetone (ACS reagent grade with a purity of 99.5%) was purchased from Sigma Aldrich Denmark. Phenol (with a purity of min. 89.0%) was purchased from VWR Bie & Berntsen. Potassium hydroxide pellets (ACS analyze grade ≥ 85.0%) were purchased from AppliChem Germany. The water used in the recycling process was distilled water supplied from Aalborg University Esbjerg.

2.2. Sub-critical water treatment

Degradation of UP resin composites was performed in a non-stirred 280-mL high pressure batch reactor constructed of 316 stainless steel (BC-1, HIP - High Pressure Equipment, USA) with an electrical heating mantle and internal Pt-100 temperature measurement device. The composite was placed in the reactor together with the solvent and additives. The reactor was then sealed and heated to the desired temperature at a heating rate of 5 °C/min. The heating was carried out by a heating mantle and a heating plate. Pressure was induced by the increasing temperature, the amount of the composite and the volume of the solvent and was maintained at approx. 300 bar throughout all of the experiments. After a reaction time of 30 min, starting after the temperature set point was

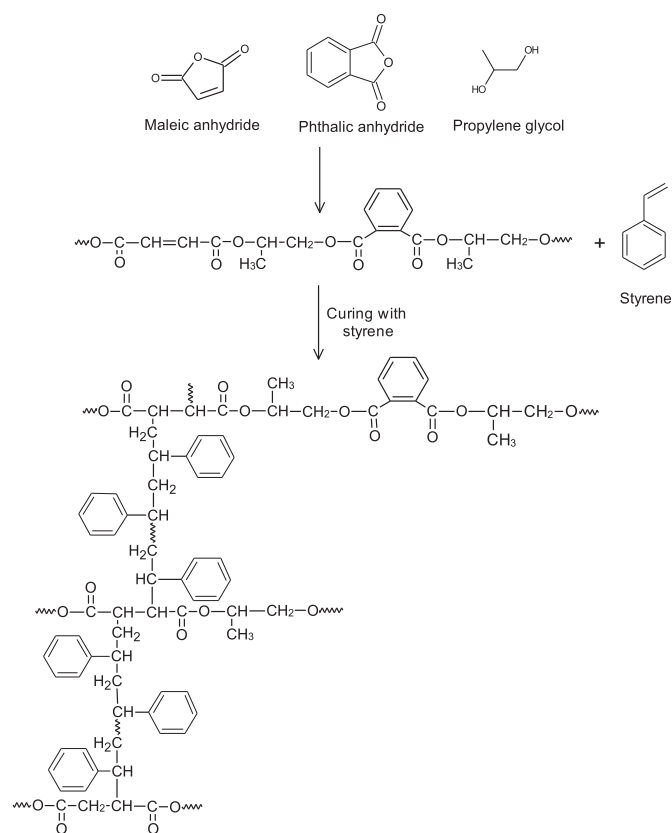


Fig. 1. Structure of UP resin pre-polymer and cross-linked UP resin.

attained, the heating mantle was removed and the reactor was removed from the heating plate. The reactor was opened after cooling to approximately 60 °C by natural convection within 2 h. To determine the effect of the temperature and the additives, the hydrolysis was carried out using the series of experiments listed in Table 1. The only controlled operating parameters were thus temperature and the additives. The ratio between the initial composite mass and water volume in the reactor was kept constant at approx. 0.3 g/mL throughout all experiments. Reaction time was also kept constant at 30 min in each experiment to exclusively evaluate the efficiency of the recycling process and the nature of the degradation products based on changes in temperature and additive blends. A fixed reaction time of 30 min was chosen based on a thorough literature research. The majority of the experiments in the field are conducted at reaction times varying between 0 and 60 min. Since it was not possible to conduct experiments with duration times in the whole region, 30 min was chosen. Furthermore, in 6 out of the 10 references in Table 1, experiments with 30 min reaction time was conducted, why it is considered as a representative reaction time. The reason for using a fixed composite/solvent ratio of 0.3 g/mL was due to the size of the composite specimens and the reactor volume, as a filled reactor was necessary, in order to easier and more precisely fix the pressure at 300 bar. In addition, composite/solvent ratios in the range of 0.02–0.5 g/mL have been used in the experiments conducted in the references shown in Table 1, why the ratio is also considered representative.

The additives were selected based on a literature research both on epoxy and polyester based composites. Blend A (no additives) has been investigated by several authors with the main purpose of degrading the resin to liberate the fibers, cf. Table 1 for references in random order. Blend B (phenol and KOH) has been investigated by Liu et al. [24]. The authors observed an increase in resin

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