

# Recycling of Glass Fiber Reinforced Composites: Can Sub-critical Water Be Used As a Reaction Medium?

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## ABSTRACT

Fiberglass is the most commonly used reinforcement in the manufacture of composite materials with polymeric matrices which are composed of organic, thermostable polyester, vinylester, phenolic and epoxy resins. Due to their cross-linked structure, recycling of thermoset composites is a particular challenge therefore they commonly end up in landfills, but the economic costs of such disposal can be very high.

The disposal of composite products in an environmentally friendly way is one of the most important challenges facing the industry and community. It is projected that the total global production of composite materials will exceed 10.3 MT by 2015, which will occupy a volume of over 60 million cubic meters. Glass fiber-thermoset matrix materials account for about 90% of all the composites currently produced which are difficult and expensive to recycle. The current cost of recycling glass-thermoset composites is not competitive against the cost of using new material.

In this study, a water-based solvolysis technology, known as hydrolysis process, was used and the reaction was carried out using sub-critical water to dissolve thermoset resin and recover the glass fibers from composites which were derived as waste from the roofage production process. After the hydrolysis, the glass fibers were obtained and a liquid fraction containing the depolymerization products of resin was retrieved. The effect of temperature (260-325 °C), time (10-120 min) and the presence of a catalyst on the recovery of glass fibers and the properties of liquid fraction were also investigated.

The glass fibers can be successfully recovered from composites at sub-critical conditions using water. However the results of the GC-MS and TOC analysis of the liquid fraction showed that the high temperatures caused the release of harmful chemicals as a result of resin degradation. Therefore the optimum conditions were elicited as 325 °C and 110 bar to recover the glass fibers, whereas the value-added compounds such as monomers of resin, benzoic acid and terephthalic acid can be recovered as well.

**Keywords:** Composites; glass fibers; sub-critical water; hydrolysis; recycling.

## INTRODUCTION

Over the past decades, production of composite materials has increased in parallel with increase of application fields such as construction, transport, electronics, civil, mechanical and biomedical engineering. Composite materials have many advantages over the conventional ones due to combining the requested properties of different materials. Among the composite materials, fiber reinforced composites (FRC) have an ample market value due to their superior characteristics in terms of weight and durability [1,2].

The most commonly used reinforcement materials in composite production are carbon and glass fiber. Glass fiber is a material made from fine fibers of glass and has properties like high strength, stiffness, high ratio of surface area to weight and dimensional stability which makes it an attractive reinforcement material for production of FRC [1,2,3].

The total global production of composites is expected to reach 10.3 MT by 2015 and the glass fiber reinforced composites accounts approximately 90 % of this production. The extensive use of fiber reinforced composites (FRC) results in an increase amount of waste including end-of-life products and unfinished products released during manufacturing processes [4,5].

Due to their complex composition (combination of polymer matrices, fibers and filler) and the cross-linked structure of thermoset resin, which does not allow remoulded, the recycling of thermoset composites is intrinsically difficult [1,5,6,7,8]. Therefore, most of the FRC wastes end up with incineration or landfill. Incineration cannot be an effective way for disposal of FRC because of inorganic content of composites which decrease the efficiency of energy recovery and the higher operational costs and the emission of toxic substances to the atmosphere which increased the environmental concerns [2,8]. Therefore, the most common way for disposal of FRC wastes is landfill. However, landfill has some handicaps like burying large volumes of materials, durability of fibers in the soil and costs associated with waste handling, transport, storage and landfill tax payments. Additionally, governments and local councils are limited or completely banning the landfill. These limitations and drawbacks are forcing the industry to find more environmental friendly ways for disposal or recycling of FRC [1,2,3,4,9].

Recycling approaches for FRC can be classified as mechanical recycling, thermal processing and chemical recycling [10]. Mechanical recycling is one of the most common and low cost methods. In this method, FRC wastes are grinding and used as filler for production of new composites [8,11]. Thermal processing includes the combustion, pyrolysis and fluidized bed applications and has high temperature requirements [1,9]. Chemical processes such as hydrolysis, glycolysis and solvolysis are carried out in a specific environment (temperature or pressure) and at lower temperatures compared to thermal processes and more efficient to recover the useful chemicals from composite matrix [1,5,8]. Chemical processes use different reaction mediums to break the bonds between matrix and fiber. In this method, using of green solvents as a reaction medium becomes important since some of the solvents can be toxic to the environment [5,11]. Chemical processes using water as a solvent are called as hydrolysis. Besides being a green solvent, water has several advantages like being cheap, recyclable, non-toxic and easy to handle. Compared to the atmospheric conditions, at sub- or supercritical region ( $T_c = 374.15 \text{ }^\circ\text{C}$ ,  $P_c = 221.2 \text{ bar}$ ), water shows both liquid- and gas-like properties and

owns lower dielectric constant, lower viscosity, higher diffusion coefficient and smaller amount of hydrogen bonds [6,8,9,11,12].

The aim of this study was to recycle the wastes of glass fiber reinforced composite production process. For this purpose, water was used as a reaction medium to depolymerize the resin and recover the glass fibers from wastes.

## **MATERIALS AND METHODS**

### **Materials**

Waste glass fiber reinforced composites were supplied from a local, composite roofage production company (Polser, Izmir).

### **Method**

Hydrolysis experiments of FRC wastes were carried out in a 100 ml stainless steel shaking autoclave. The controlled variables were temperature (260-325°C), time (10-120 min), waste to water ratio (1:5-1:20) and the presence of catalyst (NaOH). The pressure was induced by the temperature and initial volume of water. The composite waste and distilled water in desired ratios were loaded into the reactor. Then nitrogen was passed through and the system was heated by induction to desired hydrolysis temperature. The reactor was held at set temperature for required reaction times. At the end of the time, the reactor was rapidly cooled to the room temperature. After cooling, the system was opened and glass fibers were recovered. The liquid fraction was stored at 4°C following GC-MS and TOC analyses. Glass fibers were washed with different solvents and dried at room temperature. The morphology of glass fibers were examined by scanning electron microscopy (SEM).

## **RESULTS**

### **Effect of process parameters on fiber recovery**

The temperature appeared to be the most influential parameter on fiber recovery from composite wastes. The hydrolysis processes were carried out at three different temperatures (260, 290 and 325°C).

At all tested reaction times, there were no fiber recovery at 260°C. For 290°C, fiber recovery was obtained only for 120 min reaction time and 1:10 waste to water ratio. By increasing temperature from 290°C to 325°C, it was possible to reduce the reaction time from 120 min to 10 min and according to the results of the experiments at 325°C, the reaction time seemed to be less influential on fiber recovery (Table 1).

**Table 1:** The presence of fiber recovery after hydrolysis depending on the process variables

Temperature	260°C			290°C			325°C		
Time ( min )	60	90	120	60	90	120	10	15	30
Waste to water ratio (g/ml)	1:10			1:10			1:5, 1:10, 1:20		
Fiber recovery	-	-	-	-	-	+	+	+	+

At industrial scale, it is important to reduce the water requirement per unit mass of waste to increase the process efficiency and productivity. For 325°C temperature and 1:5 waste to water ratio, besides fibers and liquid fraction, solid brown particles were formed as a third phase. To prevent the formation of these solid particles, NaOH was added into reactor as a catalyst before reaction starts. Addition of the catalyst into the reaction medium seemed to catalyze the hydrolysis reaction and the particle formation problem has been eliminated.

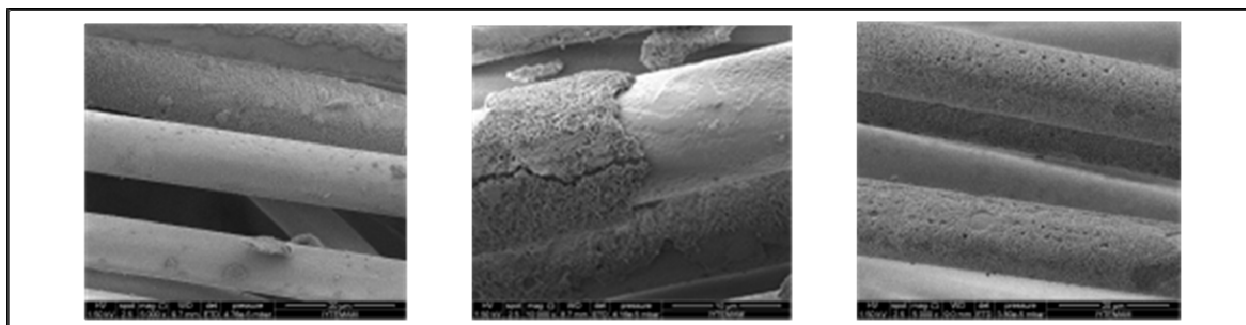
### Effect of washing solvent

After hydrolysis reaction, fibers were still coated with resin, therefore need a washing step. In this study, ethanol, acetone and dichloromethane (DCM) were tested regarding their washing effects (Figure 1).



**Figure 1:** Recovered fibers before (a) and after washing (b).

Fibers washed with acetone and ethanol, were almost completely covered with resin. DCM was found effective as washing solvent, since there was almost no resin residue on fibers. This result can be explained by the low dielectric constant of DCM compared to other tested solvents (Figure 2).



(A)

(B)

(C)

**Figure 2:** SEM images of fibers washed with DCM (A), ethanol (B) and acetone (C).

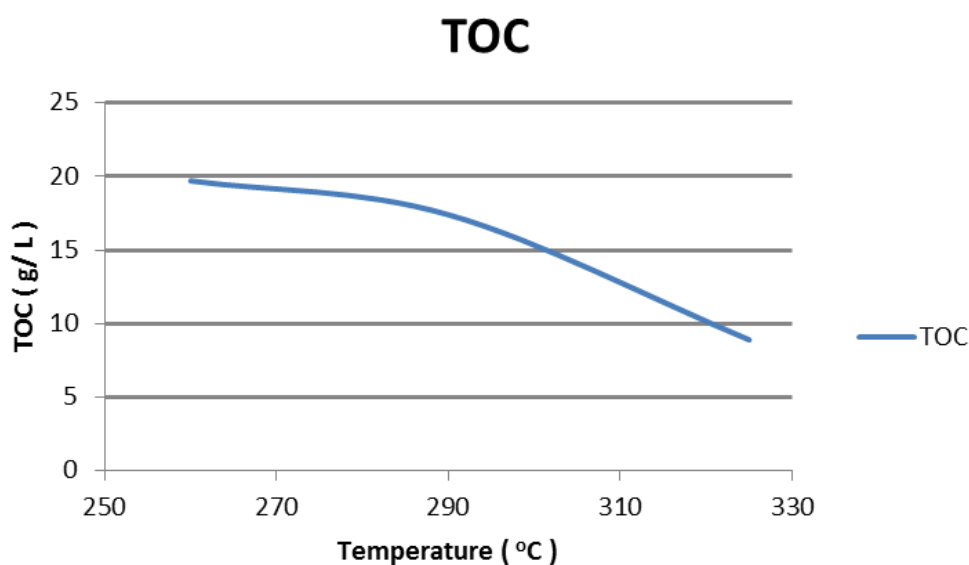
### Analyses of liquid fraction

After hydrolysis reaction, a yellow colored, homogenous liquid fraction was obtained. However, after resting for a while, precipitation of non-soluble organic substances formed a second phase. In an excellent hydrolysis reaction, only the ester bonds of polyester resin are cut and monomers of resin like glycol and carboxylic acid and also some macromolecules are formed. The GC-MS analysis showed that the liquid fraction mostly contains benzoic acid (16.13%) and phthalic anhydride (10.25%) (Table 2). Addition of catalyst to reaction medium resulted in an increase regarding benzoic acid content from 26.22 % to 60 %.

**Table 2:** Relative areas of compounds in GC-MS analysis

Compound	% Area
Benzoic acid	16,13
Phthalic anhydride	10,25
1-Phenylethanol	7,47
2-Phenylethyl formate	4,89
Neopentandiol	4,05

The TOC analyses of liquid fractions were also carried out. It was seen that the TOC value of liquid fraction was decreasing with an increase in temperature as a result of the decomposition of complex organic molecules to the simpler organic or inorganic molecules (Figure 3).



**Figure 3** : Change in TOC values depending on temperature

## CONCLUSION

The aim of this study was to evaluate the potential of sub-critical water as a reaction medium for recycling of glass fiber reinforced composite wastes. The effect of temperature, reaction time, waste to water ratio and presence of catalyst on fiber recovery were investigated. The temperature was determined to be effective on fiber recovery. The washing of fibers with an appropriate solvent was found to be necessary for removal of resin residues. The obtained resin was shown to contain plasticizer precursors such as benzoic acid and phthalic anhydride and can be valorized in composite production. Additionally, the mechanical properties of recovered fibers should be tested.

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