Thermal recycling of GFRP for marine applications

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Abstract

Composite materials have revolutionised the area of material science with high strength to weight ratio, high fatigue strength and desirable corrosion resistance properties. Glass fiber reinforced plastic with polyester resin is the most common used composite material in the field of marine industry for boat hull making. In Canada, where people enjoy spending time in the lake during summer, the boat manufacturing industry is growing year by year. At the same time disposal of old boats and vessels are also a concern. Even though there exists technique like mechanical shredding and nitric acid solvolysis, they all tend to be expensive with huge initial costs. Based on the primitive idea of separation of matrix and reusing the fiber with new matrix, a simple technique of thermal decomposition of matrix has been developed using a lab scale furnace.

Introduction

Composite material, as the name suggests is composed of two or more different materials. Usually, the fibers that form the reinforcement and the resin which binds the layers of fibers together provides excellent mechanical properties, light weight, and flexibility when it comes to product geometry. Glass fiber reinforced plastics (GFRP) where glass fibers in the form of mats reinforced with polyester have been largely used in the marine industry for making hulls and other components.

These fiberglass hulls are subjected to severe weather conditions year-round which degrade their mechanical properties. Depending on the fiber type used, due to capillary action there would be water getting absorbed and stored between the porosities of the laminate. The type of fiber i.e., long or short has significant effect of the life of the overall composites [11]. All these limits the life of mid price range fiberglass boats between 10 to 15 years. As per the Government of Canada website, there are over 6 million pleasure vessels in Canada and every year more than 43,000 vessels reach their end of life. Most of the GFRP from these vessels end up in landfills. This is mainly due to their inherent heterogeneous nature of the matrix and the reinforcement, leading to poor materials recyclability, in particular the thermoset based composites [1].

Thermal decomposition- A simple approach

Historically, In the past, researches have tried to reuse GFRP using mechanical crushing and chemical decomposition techniques [2][3]. The success rates of these techniques are dependable. Incineration of waste materials have been long suggested [1][4]. Thermal decomposition of the resin from fiber and then reusing the fiber to produce new composite laminates could be something that can have a recycling potential. Heating up the composite laminate in a furnace would be the simplest approach. Some research has been done related to pyrolysis and microwave pyrolysis of GFRP.

Thermal decomposition with fiber recovery

This process would be heating a GFRP laminate at temperatures required to decompose the resin so that fibers could be recovered and tested for reusability. The advantages of this process are low initial cost compared to other techniques and easy setup. Tests were conducted in the range of 450°C to 500°C from 10 minutes to an hour in a convection oven with an exhaust. The test would consist of laminate samples and mats which would be heated in the furnace, allowed to cool and then compared with their virgin counterparts. A laminate raw sample, a soaked laminate and glass fiber mat cut into the shape of the laminate were heat treated for 30 minutes at 500°C. Soaked sample absorbed water over 4 days time and gained 2 grams. A weight comparison table (Table 1.) is shown below and it is clear that the weight lost is of the resin during thermal decomposition as the fibers were not burned or charred.

Sample type	**Weight before (g)**	**Weight after(g)**
Raw GFRP laminate	35.02	23.4
Soaked GFRP laminate	34.2	22.85

Table 1. Weight comparison.

Figure 1 shows the laminates before and after thermal decomposition of matrix.

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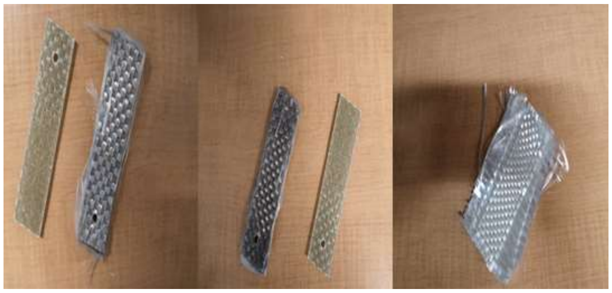

Figure 1. Soaked, raw and fiber mats after thermal decomposition

The soaked sample had less char formation compared to non-soaked sample.

Pyrolysis

Thermal decomposition in the absence of oxygen is called as Pyrolysis [1]. To obtain an inert atmosphere, nitrogen gas is pumped into the combustion chamber. Pyrolysis mainly consists of two main stages known as primary and secondary pyrolysis. Primary pyrolysis covers devolatilization (dehydration, dehydrogenation, and decarboxylation) of the main constitutes, while secondary pyrolysis involves the thermal or catalytic cracking of heavy compounds or char into gases such as CO, CO_2, CH_4, and H_2 [5]. Most of the processes include provision to condense and collect the gases produced during pyrolysis. Pyrolysis has been mainly used for biomass, but researchers are trying to study about the effectiveness of pyrolysis with GFRP composites. The main drawback of this technique is the costly setup and proper isolation of the fumes.

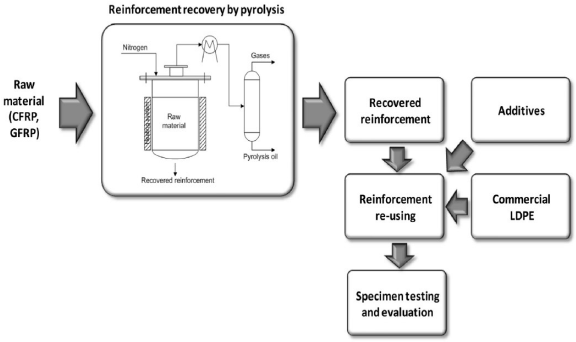

Figure 2. Pyrolysis flowchart [8].

Microwave Pyrolysis

Microwaves are normally defined as the electromagnetic waves which consist of two perpendicular components, namely electric and magnetic fields. Microwave dielectrics are known as a material which absorbs microwave irradiation, thus causing microwave heating [5]. The equipment rating for microwave pyrolysis are in the range of 3 to 4KW and 2.5GHz. Most of the pyrolysis process demand for post process purification before being reused. Pyrolysis offers the advantage of recovering both the energy and chemical value of the waste by generating potentially valuable products from the process [6].

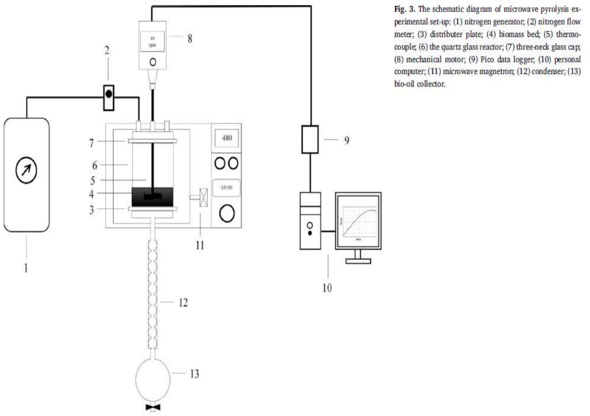

Fig. 3. The schematic diagram of microwave pyrolysis experimental set-up: (1) nitrogen generator; (2) nitrogen flow meter; (3) distributer plate; (4) biomass bed; (5) thermocouple; (6) the quartz glass reactor; (7) three-neck glass cap; (8) mechanical motor; (9) Pico data logger; (10) personal computer; (11) microwave magnetron; (12) condenser; (13) bio-oil collector.

Figure 3. Microwave Pyrolysis [7]

Experimentation of Thermal recycling and Pyrolysis

Three samples namely soaked, non-soaked and virgin glass fiber mat were subjected to thermal decomposition. Untreated virgin glass fiber mat was analysed mainly to study the deterioration in mechanical properties when subjected to high temperature. One sample was subjected to Pyrolysis in a Nitrogen environment. All the samples were re-laminated with Polyester resin mixed with Cobalt catalyst and an initiator using hand layup technique. Samples were allowed to dry for 24 hours in a fume hood.

One point to be noted is that during thermal treatment, the binding material that provides adherence of the fiber to the resin would be damaged, which could lead to lower mechanical properties. But the laminate layers were in good shape after applying 30,000Psi of jet pressure to cut them into bending sample specs on waterjet.

Figure 4. Samples for bending test

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To analyze the mechanical properties, 3 point bending test using an Instron machine was performed as per ASTM D790 standards [10].

Figure 5. Three point bending using an Instron

Evaluation of results

A virgin laminate was used as a benchmark for the test. Young's modulus (E) of all the samples were compared against that of the virgin laminate. From load vs displacement values, Stress vs Strain curve for all the samples were also plotted using the following formulas

$$\sigma = 3FL/2bd^2$$

$$\varepsilon = 6Dd/L^2 \quad \text{where}$$

F is the load in N, L is the span length in meters, b is the width of the sample in meters, d is the depth in meters and D is the elongation in meters. Table shows the values of slope of the curve, i.e. Young's modulus (GPa) for various samples.

Virgin laminate	*Non-soaked*	*Soaked*	*Virgin mat*
20.269 GPa	14.911 GPa	17.455 GPa	4.7 GPa

Table 2. Young's modulus comparison

The benchmark value obtained was 20.269 GPa from Stress strain curve shown in Figure 6.

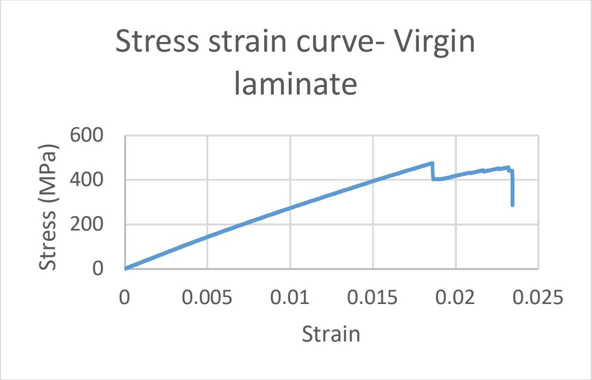

Figure 6. Stress strain curve for virgin laminate-benchmark

Soaked and non- soaked samples proved that the recycled composites could find many areas of applications, based on the test results obtained. The sample subjected to Pyrolysis had the least value of Young's modulus mainly due to irreparable delamination occurred during the process, which led to porosities between the layers. This lead to inferior bonding between the fibers and the matrix. Certain areas of the sample had visible burn marks, which all accounts for the inferior mechanical properties. One point to be noted is that samples when subjected to thermal decomposition and pyrolysis, they might have got contaminated in the furnace which could have lead to entrapped particles in the fibers. This could have lead to porosities between the fiber and resin during layup. But, Figure 4 shows that the bonding was really good for naked eye.

Virgin mat, which was subjected to high temperature showed inferior properties mainly due to the absence of proper treatment. Even though virgin mat does not account much to the area of recycling, it was tested to see the affect of high temperature on the fibers.

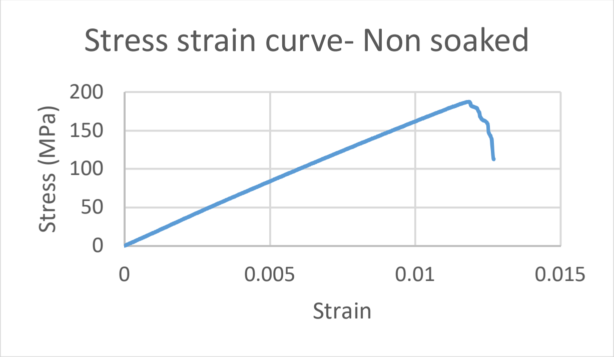

Figure 7. Stress strain curve for non-soaked sample

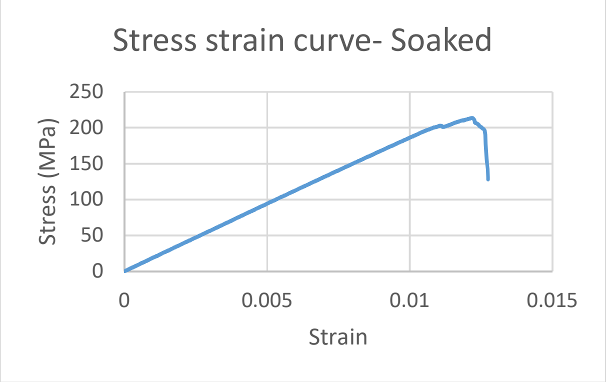

Figure 8. Stress strain curve for soaked sample

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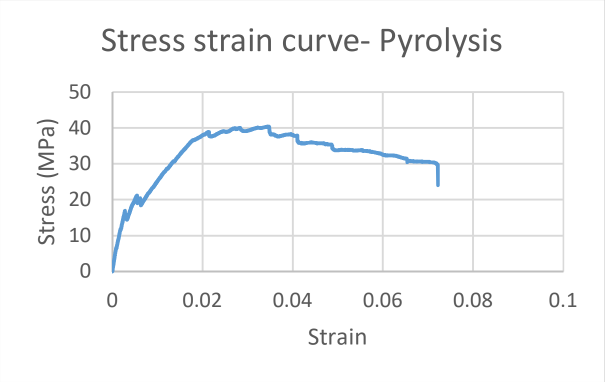

Figure 9. Stress strain curve for Pyrolysis sample

Other test values for the samples are listed in Table 3.

When compared against the benchmark values, soaked sample results were satisfactory considering the recycling potential. Soaked and non-soaked recycled GFRP could be used in non structural and cosmetic applications in the marine industry as they have desirable mechanical properties.

Test sample	*Max load (N)*	*Max stress (MPa)*	*Max extension (mm)*
Virgin sample	1690.17	475.36	0.0234
Non soaked	666.67	187.5	3.07
Soaked	**759.67**	**213.66**	**3.08**
Pyrolysis	440.17	40.42	9.97

Table 3. Max test values

To find the toughness of the samples, the area under the stress strain curve, which essentially is the energy absorbed by the material was calculated (Figure 10) and again, the benchmark was set with the value obtained for virgin laminate which was 6.724 MJ/m^3. The soaked samples, which had promising results from 3 point bending had a value of 1.488 MJ/m^3.

Conclusion

All the techniques stated above are still fresh in the area of research, but promising as they are much better compared to traditional mechanical and chemical recycling options. None of the samples were visibily burned or severely charged which promises cosmetic benefits. Compared to solvolysis and chemical recycling, absence of heavy chemical treatments like nitric acid guarantee that the fibers are not deteriorated due to chemical action.

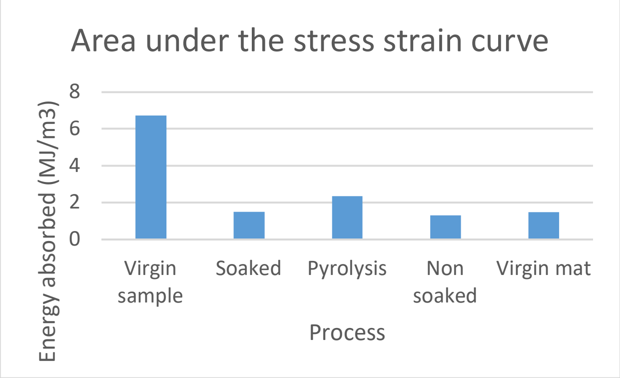

Figure 10. Area under the Stress strain curve

Even though thermal decomposition, microwave and regular pyrolysis technique are energy intensive and expensive, they yield satisfactory results with fiber recovery. To make it eco friendly, for a large boat manufacturing plant, one option is to utilize the exhaust gases or steam from processing facilities for heating up the material. These fibers could be reused for making composites for non-structural components like dashboard, consoles, trims etc. where mechanical properties are not a major concern. With future research, industries would be able to have a small recycling unit for scrap GFRP which in turn could find a new application. More research has to be done related to treatments for recycled composites which could lead to better bonding between matrix and fibers. A gel coating technique, which could be done under vacuum, could eliminate the possibility of entrapped impurities. This treatment could also include a drying agent which could remove the absorbed moisture to a certain extent, thus reducing the size of porosities. Future research could also focus on whether continuous or non-continuous fibers yield better results after thermal treatment.

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