Integrated Composite Recycling Process

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ABSTRACT

The recycling of composites on a large scale is an unsolved problem. Currently the material is either ground up into near-worthless fillers, incinerated, or digested using environmentally questionable technology; however, the vast majority of composite scrap is landfilled. Adherent Technologies, Inc. has developed a number of technologies to reclaim valuable carbon fiber and other raw materials from these composites in a potentially economically feasible manner. Since unsorted composite waste contains thermoplastic and thermoset polymer matrices, as well as contaminants like metals, paints and sealants, it is necessary to develop a unified approach that can treat all the materials at once without the need for extensive, and expensive, presorting. To achieve this, the composite waste is being treated in a three step process, including a thermal pretreatment and two wet chemical processes. The investigation of all three processes on a laboratory scale will be discussed. The high price of virgin carbon fiber is the biggest hindrance to the widespread acceptance of these important materials for applications like automotive parts. Several applications with enormous potential for economic success and environmental impact, like carbon fiber based automotive sheet molding compound, would hugely benefit from the availability of cost effective recycled carbon fiber. In addition, the new technology will greatly reduce a waste stream with exponential growth and long-term impact

KEYWORDS: Carbon Fiber Composites, Environmental/Recycling/Pollution Prevention, Materials – Chopped Fiber

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1. INTRODUCTION

Carbon fiber has become one of the most useful reinforcements for composite materials. Commonly used as long fiber, in filament winding, tape placement or fabric lay-up techniques, it is also useful as short fiber reinforcement for use in injection and sheet molding applications. Carbon fibers electric conductivity makes it of special interest for electronic enclosures and cell phone housings due to their excellent EMI shielding properties.

These properties however come with a price tag; carbon fiber, as manufactured, is at least ten times as expensive as glass fiber more commonly used in these applications. Also, there is currently a shortage of carbon fiber on the market, tightening the supply of carbon fiber for applications like chopped or milled fiber even further. Providing a cheap, reliable source of short carbon fibers is the goal of Adherent Technologies, Inc. recycling program.

ATI has studied three technologies to recycle carbon fiber from production waste and end-of-life products [1-11]. Production waste, like cuttings and overaged prepreg, is generally easily recycled, if obtained in a clean form. Unfortunately, one cannot build a recycling technology purely on the assumption of using only clean starting material. Sorting all incoming material, mostly by hand, to eliminate any contaminants, from polyethylene backing to a nail picked up with the floor sweepings, is economically not feasible. The techniques uses for production waste, like the ones for end-of-life parts, have to be able to deal with impure starting materials.

End-of-life parts, currently mostly old aircraft fuselages and wings, rocket cases and failed pressure tanks, come with additional contaminants. ATI has worked with commercial aircraft recyclers to evaluate the quality of feedstock obtainable from today’s operations. The “composite fraction” of recycled F/A 18 stabilizers was found to contain less then 50% carbon fiber composite, and had large quantities of metals, wires and other plastic materials intermingled. The goal of this study was to develop a treatment plan that can handle even this contaminated feedstock and produce a quality carbon fiber product.

ATI has investigated three different technologies of the reclamation of carbon fiber from composite waste streams. These are vacuum pyrolysis, a low temperature, and a high temperature wet-chemical process. Each technology on its own has decisive flaws, be it in the quality of the material produced, its ability to handle impurities, or its inherent cost. Combined however they can produce a top grade product at very reasonable cost.

2. EXPERIMENTAL

Fiber properties were determined via single fiber breaking tests according to ASTM 3379 on an Instron TM mechanical testing instrument. The degree of fiber purity was determined by matrix digestion according to ASTM D-3171. The analysis of the liquid recycling product was performed using gas-chromatography coupled with mass spectroscopy (GCMS) on a Shimadzu GC 17A - QP 5000 instrument.

3. RESULTS AND DISCUSSION
The ATI developed a vacuum pyrolysis unit is shown in Figure 1. The reactor is fed by a screw auger; the vacuum is maintained by the use of locks based on pinch valves. The temperature in the reactor can be adjusted via four gas-fired burners. Feed is provided via an automated conveyor, based on auger revolutions. Extensive measuring equipment for temperature and vacuum compliments this pilot scale unit.

![ATI's Phoenix reactor, a pilot scale vacuum pyrolysis unit](image)

Treating carbon-fiber based composite waste in this unit seems, at first glance, to produce a very promising product. Unfortunately, an analysis of the material shows that the purity of the carbon fiber does not quite reach the desired level of 99.5%. Scanning electron microscope examination of the fiber showed extensive char residue on the surface of the fiber. Char formation is unacceptable since it prevents good interaction between carbon fiber and resin matrix, leading to a weak composite.

The big advantage of the pyrolysis treatment is its ability to handle even the most contaminated feedstock. The treatment removes all other plastic based contaminants, allowing for an easy separation of the carbon fiber and metallic or inorganic components.

In order to produce a high quality fiber, ATI therefore started to examine wet chemical treatments. The original work [10], used a high temperature, high pressure approach. Using a heat transfer fluid and a proprietary catalyst, it was possible to produce a reclaimed carbon fiber with near-virgin properties. The material was shown to reach 99.9 % purity in digestion experiments, and SEM examination of the fibers showed no discernable difference to stock fiber. Mechanical testing, performed using single fiber tensile testing, showed a loss of less than 10% of strength compared to virgin material.
The technique, while producing superior product, proved to be very costly in scale-up attempts. The operating parameters of the unit, more than 300°C temperature and 500 PSI pressure, are outside that of common chemical processing equipment, requiring custom autoclaves and exotic valve materials for continuous operations. Also, during long term use the heat transfer liquid tented to accumulate low boiling impurities. These could further raise the pressure in the reactor vessel and required frequent removal.

ATI therefore developed a low temperature low pressure process which allowed processing in vessels built to standard chemical processing parameters, typically 150°C and 150 psi. The catalyst used in the original high pressure process was shown to be ineffective at low temperatures. With the help of a new catalyst, however, it was possible to achieve complete recycling of the carbon fiber within the parameter envelope described above. The fiber quality was comparable to the one for the original process and the process liquid could be reused indefinitely. Figure 2 shows ATI’s pilot scale composite recycling reactor.

![Figure 2. Low temperature, low pressure recycling reactor](image)

The drawback of the low temperature process lies in its limited ability to process certain types of impurities, as well as treats all composites equally. Certain high temperature composites take an extended treatment period, making a precise knowledge of the feedstock necessary.
Analysis of the fibers from the low-temperature process showed the equivalence of this treatment to the high temperature, high pressure process. The breaking strength of individual fibers reclaimed during the waste treatment is the best indicator for the quality of the fibers. Table I shows the breaking strength for fibers recovered from four different composite types as determined on our Instron TM machine.

<table>
<thead>
<tr>
<th>Fibersource</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average load at break [g]</td>
<td>13.2</td>
<td>12.3</td>
<td>14.0</td>
<td>8</td>
</tr>
<tr>
<td>Standard Deviation [g]</td>
<td>2.4</td>
<td>1.7</td>
<td>1.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The data for Runs 1 – 3 are within 10% of the theoretical breaking load of 15 g for typical virgin aircraft grade 7 µm fibers like AS4. The fibers recovered from Run 4, from the military aircraft parts, show drastically lower strength. This could be due to the use of IM7 fibers with a breaking load of 9.4 g in that program. Due to the classified nature of the components no exact information was available.

The second important fiber quality criterion is the purity of the fibers. Residual resin on the fiber surface would interfere with the bonding of resin with the fiber surface and substantially weaken any composites made from the reclaimed fibers.

The method of analysis of choice is acid digestion of the resin material and gravimetric determination of digestible parts similar to ASTM D 3171. In this test, the matrix material is dissolved by a mixture of hot sulfuric acid and hydrogen peroxide. The remaining fiber material is then weighed and compared to the starting sample weight.

Initial tests proved difficult due to fine fibers passing through the filter frittes used to collect the loose fibers. This led to results not within the ASTM prescribed standard deviation of less then 0.5 %. After washing the fibers on the filters to remove any fine material before the digestion tests, acceptable results were obtained. Typically fiber purities were better then 99%.

**Liquid Product**

We used extensive gas chromatography coupled with mass spectroscopy (GCMS) analysis of the liquid product to determine potentially valuable components. Table II shows the results of the reaction liquid analysis using computer generated compound identification.

After 5 runs of the pilot plant unit, the following composition was found for the process liquid:
Table II: Chemical Composition of Process liquid after 5 runs

<table>
<thead>
<tr>
<th>%</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>Toluene</td>
</tr>
<tr>
<td>66.7</td>
<td>Phenol</td>
</tr>
<tr>
<td>1.5</td>
<td>Isopropylphenol isomer</td>
</tr>
<tr>
<td>7.6</td>
<td>Isopropylphenol isomer</td>
</tr>
<tr>
<td>0.5</td>
<td>4-(1-Methylethyl) benzenemethanol</td>
</tr>
<tr>
<td>0.1</td>
<td>2,6 Diisopropylphenol isomer</td>
</tr>
<tr>
<td>0.2</td>
<td>Diphenyl ether isomer</td>
</tr>
<tr>
<td>0.8</td>
<td>1-(1,1-Dimethyl ethyl) 3-ethyl-5-methylbenzene isomer</td>
</tr>
<tr>
<td>5.3</td>
<td>Methyl 4-(2-phenylethynyl) benzenamine</td>
</tr>
<tr>
<td>1.0</td>
<td>unknown</td>
</tr>
<tr>
<td>0.7</td>
<td>2-[1-(4-Hydroxyphenyl)-1-methylethyl] phenol</td>
</tr>
<tr>
<td>5.4</td>
<td>4,4’-(1-Methylethylidene)bis phenol</td>
</tr>
<tr>
<td>3.3</td>
<td>4-(3,4-Dihydro-2,2,4-trimethyl-2H-1-benzopyran-4-yl)phenol</td>
</tr>
</tbody>
</table>

This composition is very similar to the composition observed in the high temperature recycling process, where extensive studies have shown a potential of the liquid as a raw material for making phenol-formaldehyde resins. One exception to this is the presence of an amine compound, probably due to the last run using a polyurethane resin, which contains a large amount of nitrogen compounds. By treating the hydrocarbon product at high temperatures after removal of the catalyst, all potentially hazardous amine compounds can be decomposed.

4. CONCLUSIONS

The solution to the overall problem is the combination of the three processes. In the first step, the contaminated feedstock is treated thermally under vacuum. This removes plastic contaminations, as well as all volatile components. With the removal of the plastic components, metal and inorganics can then be easily separated before the wet chemical treatment. This saves processing chemicals and clean-up costs. It also preprocesses the composite fraction, partially breaking up the matrix resin and allowing for easier access for the liquid during the wet chemical treatment. By avoiding temperatures high enough to char the carbon fiber the carbon fiber quality is not compromised.

The matrix of the composite is then removed using the low temperature, low pressure process. This is the most economical method of reclaiming the carbon fiber. Since most impurities are removed in the pretreatment step, the consumption of chemicals is minimal. The addition of a high efficiency centrifuge to separate fiber and liquid has shown to also remove the requirement for repeated washing of the fiber product. A single rinse with acetone, which is consequently recycled, is sufficient to clean the fiber.

Any unreacted matrix material from unusual feedstock can then be removed in a final high temperature treatment. Since this step only needs to remove traces, it can be added to the process economically by using only small quantities of treatment liquid. Since no more low boiling material is formed, the liquid does also no longer need to be purified between treatment cycles.
5. ACKNOWLEDGMENTS

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6. REFERENCES


