On the Recycling of Carbon Fibers Reinforced Polymer Matrix Composites

FLORIN TEODORESCU, HORATIU TEODORESCU, GRIGORE STANCA, DUMITRU CONDURACHE, RADU STEFAN CRACIUNOIU
Mechanical Engineering Research Institute ICTCM SA
103 Oltenitei Blvd., 041303 Bucharest
Department of Mechanical Engineering
Transilvania University of Brasov
29 Eroilor Blvd., 500036 Brasov
ROMANIA

Abstract: - The paper presents some direct and primary recycling methods of carbon fibers reinforced polymer matrix composites used in automotive industry as “high volume” components (i.e. dashboards, engine manifolds), composite bodies and structural parts in sport cars, composite bodies and parts in “low volume” applications. Some recovering possibilities of carbon fibers reinforced recycled composite materials are also described. The composite disintegration can be realized through pure mechanical methods (like selective shredding) or by pyrolytic ones. Even the carbon fibers can be shredded up to a certain point. A possible recovering of carbon fibers could be the manufacture of electric conductive plastic materials (for instance, for electromagnetic compatibility) or as filler in mixtures used as anti-friction layers, for instance the automobiles brake plates.

Key-Words: - Recycling, Carbon fibers, Polymer matrix composites, Thermosetting resins, Direct recycling methods, Primary recycling methods, Hadeg Recycling, TZN process

1 Introduction
Carbon and graphite fibers are produced by controlled oxidation and carbonization of some selected organic fibers, i.e. so called precursors like cellulose, polyacrylonitrile (PAN), lignin and pitch. The carbon fibers properties are influenced both by fibers raw material and the precursor fiber quality as well as the used manufacturing technology.

Oxidization and carbonization at temperatures up to 1600°C produces a high strength fiber and graphitization by increasing the temperature to 3000°C produces a high modulus graphite fiber (fig. 1). Advantages of carbon/graphite fibers are: high resistance to fatigue and creep; good resistance to wear; good properties of vibration damping; thermal stability; high long-term resistance to corrosion; good electrical conductivity and permeability to X-rays.

The latest types of fibers offer lower fuzz and greater spreadability [1], [2], [3]. The resulting fibers are stronger than steel, stiffer than titanium and lighter than aluminium. Carbon fibers exhibit the highest specific stiffness and very high strength both in tension and compression. Their impact strength is lower than that of glass or aramid fibers, so that carbon fibers are often combined with these to form hybrid laminates. Continuous carbon fibers can be combined with almost all thermoset and thermoplastic resins and are used for braiding, weaving, filament winding and prepreg manufacture.

Chopped fibers are used in molding compounds for compression or injection molding, resulting parts with high resistance to corrosion, creep and fatigue, with high strength and stiffness. The usual types of carbon fibers are high strain (HS), high tenacity (HT), high modulus (HM) and intermediate modulus (IM). Table 1 shows the effect of precursors on the properties of carbon fibers. Advanced fibers reinforced polymer matrix composites can be recycled using direct- (mechanical shredding) and primary recycling methods (pyrolysis and solvolysis).

2 Direct Recycling Methods
Carbon fibers reinforced polymer matrix composites are seen as materials that can not be recycled or can be partially recycled. Here we can distinguish between carbon fibers reinforced thermosetting resins and carbon fibers reinforced thermoplastic resins. The composite systems with thermosetting resins can not be re-melted, so a recycling system of
these materials will show different as a recycling system of thermoplastic composite materials.

![Diagram](chart.png)

**Fig. 1. The schematic production process of carbon fibers**

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Fiber diameter [μm]</th>
<th>Tensile strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN (C-fibers)</td>
<td>8.8</td>
<td>3300</td>
</tr>
<tr>
<td>PAN (graphite fibers)</td>
<td>6.6</td>
<td>2600</td>
</tr>
<tr>
<td>Cellulose</td>
<td>10.15</td>
<td>2000</td>
</tr>
<tr>
<td>Lignin</td>
<td>-</td>
<td>600</td>
</tr>
<tr>
<td>Hydrocarbon pitch</td>
<td>10.5</td>
<td>1030</td>
</tr>
</tbody>
</table>

**Table 1. Effect of precursors on the properties of carbon fibers [1]**

Small amounts of uncured prepregs made from epoxy resins reinforced with carbon fibers are processed by Hadeg Recycling and brought, as a result of the process, under the form of a recycled material. The processing methods were carried on a two steps shredding unit (fig. 2). The unit capacity is of about 3 – 4 t/month recycled material. In the first stage, the protection foils are manually removed.

After this, the uncured laminates are cured in an infrared oven. In the next step, the cured prepreg pieces are primary shredded in a shredder. By help of a hammers mill with 4 mm round sieves, the wastes are shredded at grains average value of 200 – 700 μm. The material shredded in the hammers mill is not further processed. Nowadays, every month, about 500 kg recycled material is reused in polymeric compounds and ceramic materials. The introduction of recycled material in thermoplastics have been accomplished in extruders with double snails. The shredded material in direct recycling methods can be used for instance as recycled material for the new Sheet Moulding Compounds (SMCs) [4].

![Diagram](hadeg_recycling.png)

**Fig. 2. Schematic representation of Hadeg Recycling Unit [5], [6]**

For a structural SMC material which contains both glass- and carbon fibers, the high frequency impulses technique HLPT have been tested, as preparation process for recycling. The final aim is to separate the matrix, fibers and fillers from a SMC material. At this process (usually called TZN), two electrodes charged from a battery lie in a liquid (fig. 3), [5].

During charging, between electrodes appear an electric arch which forms a pressure wave in liquid. Pressures between 500 – 1000 bar appear in a time period of about 10 μs.

At the TZN process there is a wet and a dry variant. At the wet variant the material which will be shredded lies in liquid whereas at the dry variant the shredding is accomplished by help of a membrane which protects the composite material from liquid.

Finally, the shredded SMC material have been treated with liquid nitrogen so that it should be in a...
brittle status, much easier to disintegrate. The separation on fractions of shredded material can be subsequently done through selection according to ERCOM process [7].

The TZN process has been partially modified at the Mechanical Engineering Research Institute ICTCM SA Bucharest in co-operation with Transilvania University of Brasov and COMPOZITE Ltd., Brasov, Romania and applied at an experimentally pilot unit.

3 Primary Recycling Methods

The primary recycling processes are pyrolysis and solvolysis. These have the aim to remove the matrix from the cured thermosetting material. At primary processes, the matrix materials disintegrate under the influence of heat and pressure with the aim to remove completely the matrix from fibers without affecting fibers properties [8 – 14].

To accomplish a complete disintegration of epoxy matrix, a carbon fibers reinforced material have been pyrolized for 4 hours in a rotating oven and another 2 hours at 450°C. In these conditions, the matrix remainders could be completely burned and individual elastic fibers have been obtained, fibers that came easy undone from the fibers bundle [15], [16], [17], [18].

4 Results

Carbon fibers reinforced recycled composite materials can be reused as thermoinsulating plates for interior clothing of high temperature ovens, electrode type plates, filler in mixtures used as anti-friction layers, for instance the automotives brake plates.

To manufacture these brake plates a lot of materials must be incorporated such as fibers, metals, fillers, binders (phenolic resins and synthetic rubber). Other application include carbon fibers reinforced concrete. For this purpose, only fibers having pitch as precursor can be used. In constructions, carbon fibers reinforced recycled composite materials can be reused as tiles, plates, beams and joints, strong, light and thin carbon fibers reinforced concrete plates.

For instance, the mechanical characteristics of carbon fibers reinforced concrete are presented in table 2. Carbon fibers based on pitch with diameters between 18 μm and 3 mm have been used.

Table 2. Features of carbon fibers reinforced concrete

<table>
<thead>
<tr>
<th>Fibers volume fraction [%]</th>
<th>Tensile strength [MPa]</th>
<th>Strain at maximum load [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.44</td>
<td>0.047</td>
</tr>
<tr>
<td>1</td>
<td>4.75</td>
<td>0.065</td>
</tr>
<tr>
<td>2</td>
<td>6.44</td>
<td>0.126</td>
</tr>
<tr>
<td>3</td>
<td>7.10</td>
<td>0.220</td>
</tr>
</tbody>
</table>

Fig. 3. Schematic representation of TZN process [5]
Unlike glass fibers, the great advantage of carbon fibers reinforced concrete is that the carbon fibers have not been attacked by the alcali medium developed in concrete.

5. Conclusions
Regarding the reusing of the raw materials of carbon fibers reinforced composites, the matrix removal (composite disintegration) can be accomplished with the aim to regain and reuse the high strength fibers. The composite disintegration can be realized through pure mechanical methods (like selective shredding) or by pyrollitic ones. Even the carbon fibers can be shredded up to a certain point.

A possible reusing of carbon fibers could be the manufacture of electric conductive plastic materials (for instance, for electromagnetic compatibility). Regarding the thermal reusing of carbon fibers reinforced composites, this is problematic since the carbon fibers can not be completely thermic disintegrated by means of oxygen or through decreased contribution of oxygen.

A disadvantage of thermal reusing of carbon fibers is that the ejected air that contains incomplete disintegrated carbon fibers could block up the filters. Even at ERCOM recycling process, the shredded carbon fibers can be reused at reinforcing of thermosetting composite materials. In ERCOM process is possible a joint shredding of glass fibers and carbon fibers reinforced composites.

References: