Recycling carbon fibre: State of the art and future developments

Anthony Stevenson, Technical Manager
Outline of presentation

- Why recycle?
- Recycling methods
- The development of recycled carbon fibre products for the compounding and composites industries
- Test results, comparisons with current materials
- Examples of applications
Why Recycle

- **COST**
  - Recovery of fibres requires much less energy than production of virgin fibres

- **Security of supply**
  - Demand for virgin fibre expected to exceed supply in 2018 so primary producers may be selective when meeting orders

- **Legislation**
  - EU Landfill directive 99/31/EC
Life Cycle Analysis

- Pyrolysis consumes <10% energy needed to produce virgin carbon fibre
Carbon Fibre Demand

Global demand (kT) for carbon fibre [1]

Expected CAGR 2014-2021 = 12%

## Carbon Fibre Supply

<table>
<thead>
<tr>
<th>Year</th>
<th>Nameplate capacity (kT)</th>
<th>Effective capacity (kT)</th>
<th>Expected demand (kT)</th>
<th>Spare capacity (kT)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>109</td>
<td>65.3</td>
<td>44</td>
<td>21.3</td>
<td>2</td>
</tr>
<tr>
<td>2014</td>
<td>125</td>
<td>79</td>
<td>53</td>
<td>26</td>
<td>1</td>
</tr>
</tbody>
</table>

- Forecasts vary, plant efficiency & availability can change
- Might be a problem with shortage of supply
- Majority of CF production in USA & Asia

Types of Carbon Fibre waste

- **Dry fibre waste**
  - Bobbin ends
  - Selvedge
  - Offcuts from ply cutting
  - Off-spec material

- **Cured waste**
  - Trimmings
  - Swarf
  - Off-spec material

- **Pre-preg waste**
  - Offcuts from ply cutting
  - Out of life material
  - Off-spec material

- **End of life waste**
  - Will be significant in years to come
Contamination in Carbon Fibre waste

- Glass fibre
- Metal
- Mineral fillers
- Release paper/film
- Honeycomb, foam
- Paints, surfacing films
- Foreign objects
Quantities of waste (2015)

Carbon fibre waste (tonnes) from manufacturing

Total: 24,000 tonnes
Lots of aerospace grade pre-preg offcuts

No need to worry about taking contaminated EoL

24,000 tonnes is about the difference between demand & supply predicted by ORNL for 2020
Recycling processes

- **Mechanical**
  - Regrind & reuse: thermoplastic recycling process

- **Pyrolysis: Thermal decomposition of matrix**
  - Pyrolysis followed by oxidation
  - Mixed mode
  - Choice of furnace types

- **Solvolysis: Chemical dissolution of matrix**
  - May require hazardous chemicals
  - May require elevated pressure & temperature
Solvolysis processes

- Boiling concentrated nitric acid will decompose resin
  - ISO 14127
  - Not employed commercially
- Supercritical mix of acetone/water at 320 °C, 170 bar decomposes resin fully within one hour
  - No fibre damage
  - Chemical “soup” can be distilled & value recovered
  - Risks in scale up
- Some resins designed for solvolysis (Adesso)
Inert atmosphere pyrolysis

- Waste material loaded into pressure vessel
- Vessel evacuated and/or purged with inert gas
- Heated to about 500 °C to decompose resin
  - No risk of oxidative damage so can handle thick sections
- Resin volatilizes to give “pyrolysis oil”
  - Can be distilled to recover chemicals or burnt for energy
- Some char on fibres (may require a later oxidation step)
- Batch process
Pyrolysis with oxidation

- Waste material loaded onto belt
- Heated to about 500 °C to decompose resin
  - Resin ignites & depletes oxygen
  - Char is oxidized much faster than fibres
  - Gases cleaned in afterburner
- Continuous process
- “Black Art” in atmosphere control
Fibre Properties

- Oxygen levels in furnace controlled to burn off char
  - Don’t intend to damage fibre
  - Fibre maintains stiffness but loses some strength
  - Fibre desized
- Recovered fibres are not well aligned
- Single fibre testing employed
  - Very fiddly!
  - High coefficient of variation
  - Need longish fibres for test
Fibre Mechanical Properties

- Reclaimed carbon fibres have similar mechanical properties to the original fibres (results do vary with the type of feedstock).
Fluidised bed process

- Coarsely ground waste fluidized by hot air
- Liberated fibres carried out
- Cyclone sorts fibres by mass (dust is not collected)
- Dense contaminants fall through bed
- Good for short fibres (under 25 mm)

“Developments in the fluidised bed process for fibre recovery from thermoset composites”, Pickering, S.J. et al in: 2nd Annual Composites and Advanced Materials Expo, CAMX 2015; Dallas, 26-29 October 2015
Fibre alignment

- All recovery processes yield discontinuous fibres
- Low bulk density, difficult to handle
- Intermediates:
  - Pellets
  - Papers
  - Textiles (e.g. carding)
  - Yarns/tapes
Milled Fibre: Carbiso MF

- Short fibre, MF100, mean length = 0.1 mm (MF80, 0.08 mm)
- Strength high: fibre breaks at weak points during milling
- Stiffness virtually the same as virgin fibre
- No surface coating so bonds well to thermoplastics
- Low CTE
  - Axial: -0.4 x 10^{-6} m/m/K
  - Transverse: 15 x 10^{-6} m/m/K
- Thermal conductivity = 5.4 W/m.K
- Not respirable – no diameter reduction in milling
- Working on pelletised form for easy dosing
Injection moulding

- Chopped fibres fed into side feeder of extruder
  - Fibre bridges during feeding
  - Fibre breaks during kneading
  - Fibre clumps block die
- Scale up needs more work
- Possible to make pellets for injection moulding (right)

**Diagram:**
- **Polymer Granulate**
- **Pre-Chopped Fibres**

Chopped extrudates ready for inj. moulding

**Image:**
- Black granules with a scale of 10 mm
Injection moulding: PA66

- No significant difference between virgin & rCF
- 10% carbon gives same stiffness as 30% glass

Recycled CF: ALCOM MP PA66 70x0 15100-3 CF
Prime CF: ALCOM PA66 910/1.1 CF10/20/30
Glass filled CF: ALTECH PA66 A 2030/106 NC0001-00
Injection moulding: PA66

- No significant difference between virgin & rCF
- 10% carbon approaching strength of 30% glass

Recycled CF: ALCOM MP PA66 70x0 15100-3 CF
Prime CF: ALCOM PA66 910/1.1 CF10/20/30
Glass filled CF: ALTECH PA66 A 2030/106 NC0001-00
Injection moulding

- For PA66 compounds see 21% reduction in density for the same mechanical properties
- Compound with 10% rCF is only 2% more expensive than compound with 30% glass
- Increased cost justified by weight saving
- No need to re-engineer tools
- Win-win!

Thank you to Albis for producing compounds, moulding and testing sample bars, and giving permission to report the data
Paper making processes

- In paper making fibres are dispersed in water
- Slurry discharged onto belt/wire & water removed
- e.g. process used by Technical Fibre Products to make veils
- In the Hiperdif process jets of slurry are directed at a series of plates so the fibres are aligned
- Produces aligned tape from short fibres

Non-wovens

- Fibres recovered as discontinuous fibres
- Chop to manageable size
- Card to form web
  - Carding pyrolysed (de-sized) CF is not straightforward
- Cross-lap to control thickness & gsm, or create sliver for yarn spinning
- Can blend in other fibres (thermoplastic)
ELG products

- Carbiso M
  - 100% rCF mats
  - Can be made from sized fibre (epoxy)
  - Used in thermoset moulding processes

- Carbiso TM
  - Blends of rCF with thermoplastic fibres
  - PP, PA6, PA66, PPS, PET etc.
  - Generally compression moulded

- Weights 100 - 500 gsm; widths up to 2.7 m
### Mechanical properties: RTM

- Epoxy resin, 110 °C, small gap during injection
- Normalised to 35 vol% CF

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Test Direction</th>
<th>SGL Recatex Isotropic</th>
<th>SGL Recatex Oriented</th>
<th>ELG Weaving Waste</th>
<th>ELG Pyrolysed Prepreg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tensile Strength (MPa)</strong></td>
<td>Cross Web</td>
<td>198</td>
<td>289</td>
<td>382</td>
<td>340</td>
</tr>
<tr>
<td><strong>Tensile Modulus (GPa)</strong></td>
<td>Cross Web</td>
<td>24.5</td>
<td>31.5</td>
<td>34.1</td>
<td>40.1</td>
</tr>
<tr>
<td><strong>Tensile Strength (MPa)</strong></td>
<td>Roll</td>
<td>164</td>
<td>123</td>
<td>215</td>
<td>168</td>
</tr>
<tr>
<td><strong>Tensile Modulus (GPa)</strong></td>
<td>Roll</td>
<td>19.3</td>
<td>13.1</td>
<td>18.7</td>
<td>19.3</td>
</tr>
</tbody>
</table>
Mechanical properties: pre-preg

- Epoxy pre-preg made (see schematic)
- Left to mature 24 h room temperature
- Compression moulded, hot in hot out
- 150 C, 2 MPa, 5 min
Mechanical properties: pre-preg

<table>
<thead>
<tr>
<th>Test Direction</th>
<th>longitudinal</th>
<th>transverse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>250</td>
<td>340</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>24</td>
<td>35</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>-</td>
<td>600</td>
</tr>
<tr>
<td>Flexural Modulus (GPa)</td>
<td>-</td>
<td>52</td>
</tr>
</tbody>
</table>

- Laminates moulded from pre-preg 10 minutes at 155 °C with 2 MPa applied pressure. Hot in hot out.
- Carbon fibre volume fraction = 35%
Hybrid non-wovens

- Carbon & thermoplastic fibres intimately mingled
  - Short flow distance for melt
- Direct moulding:
  - Die cut fabric to shape & load into mould
  - Heat to > Tm (mould may be preheated)
  - Apply pressure to consolidate material
  - Cool to below Tg
- Preconsolidated sheet
  - Preheat to around $T_m$
  - Load into chilled mould
  - Apply pressure to deform sheet before it freezes
## Hybrid non-wovens

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>CF-PA6 Cross-plied</th>
<th>CF-PP transverse</th>
<th>CF-PP longitudinal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/cc</td>
<td>1.35</td>
<td>1.27</td>
<td>1.27</td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>MPa</td>
<td>227</td>
<td>204</td>
<td>159</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>GPa</td>
<td>21.7</td>
<td>15.6</td>
<td>13.5</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>MPa</td>
<td>273</td>
<td>154</td>
<td>161</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>GPa</td>
<td>17.7</td>
<td>18.0</td>
<td>18.6</td>
</tr>
</tbody>
</table>

- Tests conducted on compression moulded panels 2 mm thick
- Carbiso mats made on laboratory line 40 wt% CF
Applications: Carbiso M

iStream™ Carbon Concept

- Primary structure: steel tube design
- Secondary structure: rCF panels of Carbiso M and thermosetting resin

courtesy of Gordon Murray Design
Applications: short fibre

**SMC and BMC moulding compounds** used in areas where long fibres cannot conform to complex geometry or where there are exacting surface quality requirements.

**Net shape manufacturing**
Chopped fibres being used in several research projects investigating net shape manufacturing processes--preforming for resin transfer moulding or stamp forming applications.
Outlook

- Recycled carbon fibre can change supply/demand equation
- Security of supply with controlled quality
- Carbiso TM and Carbiso M materials being trialed by a number of automotive and aerospace Tier 1s
- Huge market for short fibre rCF in thermoplastics, (once manufacturing issues solved)
Any Questions?

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