Carbon Nanotubes: Applications and Benefits in the Automotive Industry
Nanocyl SA at a glance

- Founded in **2002**, Headquarter in Sambreville, BE
- **50 people** (80% TS, R&D, Manufacturing)
- 2 sites: Essor & Vacherie, Sambreville
- **460 MT** of industrial **MWCNT** capacity, more than **3500 MT** of thermoplastic compound capacity
- International certifications: **ISO 9001 & RoHS**
- **A growth y-o-y of % (GM) >20%**
- More than 55% Sales is NC7000; rest is formulated products: Thermoplastics, Thermosets, Dispersions (Water or Solvent),
- Sales in: Energy (batteries), Electronics, Automotive, custom-Industrial, Utilities, Medical, etc…

« RoHS » : Restriction of the use of certain Hazardous Substances in electrical and electronic equipment
History and milestones

Foundation of a spin-off from the Universities of Namur and Liege in Belgium

Investment in CNT pilot plant unit

Demonstrated industrial production of CNTs

Move from lab to the industrial production

Industrial unit of 40 mt of NC7000™

Compounding units >3500 mt capacity high temperature thermoplastics

Stretching of the industrial unit to > 60 mt of NC7000™

Industrial unit of 400mt of NC7000™

1st commercial use of NC7000™ in automotive

Launch of Plasticyl™

Transfer to current location in Sambreville, Belgium

1st commercial use of NC7000™ in electronics

Location of nanocyl in Namur University in Belgium

Start of US & Korean presence

Launch Sizicyl™, Pregcy™, Biocyl™

Extension of the Plasticyl™ product range

Launch Epocy™, Thermocyl™, Aquacyl™

1st sales in Batteries

1st sales in A-F Marine

Key:
- Production
- Products
- Structure
- Markets

ECOLOGY OF COMMERCIAL USES
Electrical Conductivity
The electrical conductivity of CNTs is much higher than copper, allowing non-conductive plastics to be turned into conductive materials.

Mechanical Strength
Thanks to their high elasticity and excellent tensile strength, carbon nanotubes exhibit a mechanical strength which is 5 times higher than steel – at only a quarter of the specific weight.

Thermal Conductivity
CNTs beat the thermal conductivity of the best natural thermal conductor of all – diamonds.

Flame Retardancy
Carbon nanotubes have the ability to promote flame retardancy at very low filling levels thanks to the formation of a thermal insulating and low permeable char.
Key benefits at a Glance

- **Total Cost Benefits Thanks to Breakthrough Performances**
  - Lower loading required compared to conventional materials (carbon black, carbon fiber,…)
  - Improved recyclability
  - Higher mechanical retention allowing innovative and thinner features
  - Higher electrical conductivity for emerging applications
  - Higher cleanliness cuts manufacturing losses and OEM product recalls
  - Better abrasion resistance makes plastic components last longer

- **Optimized and Easy Processing**
  - Superior flowability of CNT based compounds enable more complex mold designs
  - Custom grades exclusively developed for specific applications and processes (EBM, TPU,…)
  - Increased yield on throughput
  - Worldwide technical support to help OEMs & compounders successfully develop innovations

- **Improved Sustainability**
  - **Weight Reduction** – lower greenhouse gas emissions (automotive parts,…)
  - **Energy Saving** – Generating more efficient energy-storage solutions (batteries,…)
  - **Toxic Components Replacement** – Getting rid of toxic components (Anti-fouling, Halogen-free)
  - **Recyclability** – Improving the applications’ recyclability (electronic packaging,…)
  - **Future Developments** – Air & waste water treatment
Importance of processing parameters: Compounding steps
Percolation vs Mixing - Illustration

1. Disperse
2. Connect
3. Migrate

AGGLOMERATE

Poor Mechanical Properties
Decent Mechanical Properties

Conductivity

SHEAR RATE

mild mixing
robust mixing

SHEAR RATE
Torque & pressure decreases linearly with temperature.

Torque decreases with increasing CNT%.
- Flow reorientation of CNT increase flow orientation of polymer chain.
- Anisotropy of CNT tube plasticises polymer chain during shear flow.

Pressure increase a bit with increasing CNT%.
- Better melt strand stability, given by small increase in die pressure.
- Increase in pressure is small, no effect on throughput.

Ramification: Introduction of CNT at less than 5wt% actually helps to increase throughput. This is contrary to popular believe that CNT causes reduction in throughput.
Torque decreases linearly with screw speed up to 300 rpm, then level off.
- possibly maximum shear thinning or full chain stretch or alignment reached at 300 rpm.

Die pressure reduces a little until 300 rpm, then level off.
- same reason as above.

**Ramification**: CNT improves melt shear thinning effect.
In another word, introduction of CNT actually improves processability.
Temperature vs. Conductivities

Lower transition

Upper transition
Quality, intrinsic properties and cost price of the carbon nanotubes are different among manufacturers and are dependent on raw materials used (catalyst) and on the production process (reactor).

Because of Nanocyl’s unique catalyst composition and reactor, both protected by international patents, Nanocyl is able to offer carbon nanotubes:

- with the best electrical properties on the market, leading to lower loading required compared to its competitors
- with a cost advantage over its competitors
Importance of processing parameters:
Converting compounds
Combine surface quality and conductivity

- Decrease injection speed to improve conductivity
- Increase Mat. Temp. to improve conductivity
- Antagonist effect !!!
- Increase injection speed to improve surface quality
- Decrease Mat. Temp. to improve surface quality
Combine surface quality and conductivity

Calculation of optimization according factorial design

- Minimize clear spots (target = 0, upper value = 0.5)
- Minimize pinholes (target = 0, upper value = 0.5)
- Minimize SR (target = 1E+03 Ohm.sq, upper value = 1E+06 Ohm.sq)
- Minimize VR (target = 1E+01 Ohm.cm, upper value = 1E+04 Ohm.cm)

<table>
<thead>
<tr>
<th>Injection speed</th>
<th>Mold temperature</th>
<th>Material temp.</th>
<th>Plast. speed</th>
<th>Back pressure</th>
<th>Holding pressure</th>
<th>Holding time</th>
<th>SR</th>
<th>VR</th>
<th>Pinholes</th>
<th>Clear spots</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm³/s</td>
<td>°C</td>
<td>°C</td>
<td>m/s</td>
<td>bars</td>
<td>bars</td>
<td>s</td>
<td>Ohm.sq</td>
<td>Ohm.cm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>120</td>
<td>300</td>
<td>0.4</td>
<td>40</td>
<td>450</td>
<td>8</td>
<td>7 E+03</td>
<td>8 E+01</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Recommendations:
- Mold temp: max (120°C)
- Mat temp: max (300°C)
- Injection speed: medium

Model and parameters validated!

Perfect surface finish and high level of conductivity just with good injection molding parameters!
Automotive applications
ESD Critical Parts in Fuel Systems

<table>
<thead>
<tr>
<th>Component</th>
<th>Acetal</th>
<th>PPS</th>
<th>PBT</th>
<th>HDPE</th>
<th>HT PA</th>
<th>PA 6/6</th>
<th>PA 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel filler pipes</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Fuel lines</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Fuel pump components</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quick connectors</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>
Injection molding application: Fuel pump

Conductive additive for fuel lines

- Meets SAE J1645 standards
- Weight reduction of automotive parts
- Allow innovative designs, due to easier processing of Nanocyl compounds
- Dimensional Stability & Creep resistance
- Cost competitive solution
- Nanocyl CNTs impart electrical conductivity at a lower loading
Injection molding application: Fuel pump

Plasticyl POM1001 - Typical Performance after dilution and Injection Molding

<table>
<thead>
<tr>
<th></th>
<th>2%WT</th>
<th>3%WT</th>
<th>5%WT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume resistivity Ohm.cm</td>
<td>5</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Surface resistivity Ohm/sq</td>
<td>540</td>
<td>46</td>
<td>10</td>
</tr>
</tbody>
</table>

NC7000 can be used to develop fuel pump solution:

- Approved in automotive fuel pump systems
- With SR < 10^3 Ohm.sq at very low loadings (<2.5 wt%)
- Fully complying with SAE J 1645 recommendation
- Resistant to aggressive chemicals in fuels (Fluid L,C, RME,SME) (retention of electrical properties)
- Clean (no leaching of additives, NC7000 fully embedded in matrix)
- Cost, weight and energy saving
- With good long term creep behavior
- With same friction property as based POM
- Fully recyclable
- Compatible with standard process equipment
Quick Connectors in Fuel Systems

- Electrically conductive PA
- Keeping PA properties offering ESD and conductive properties
- Conductivity not sensitive to fuel contact, fluid L, C, etc.
- Meets SAE J 1645 standards
- Fits existing machinery/tooling
- Tailor-made properties thanks to tailor-made products
In addition of excellent retention of SR, PA12/NC7000 composites present excellent retention of mechanical properties (pull apart and insertion force as well as impact resistance).

Nanocyl can provide injection molding guidelines to get the best surface conductivity in combination with the best surface quality.
Quick Connectors Basic Requirements
Immersion in Fuel/ Insertion Force / SAE J 2044

Max acceptable insertion force 111N (PA 12 30%GF)

Easy to insert – Keeps elasticity and flexibility properties
Quick Connectors  Basic Requirements
Immersion in Fuel / Pull Apart Force/ SAE J 2044

Min. acceptable pull apart force 297 N (PA12 30% GF)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Min pull apart force</th>
<th>Max pull apart force</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85</td>
<td>10</td>
</tr>
<tr>
<td>CE</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>CP</td>
<td>85</td>
<td>10</td>
</tr>
<tr>
<td>CE</td>
<td>85</td>
<td>10</td>
</tr>
<tr>
<td>85</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Pull apart forces measured immediately after taken out of fuel, 48h dried values same level but in lbs, therefore not considered here

Strong connection – Keeps the tube in place
Impact resistance test

High conductivity and mechanical performance! No contradiction
Injection molding application: Filler system application (HDPE)

Addition of NC7000 can impart excellent surface resistivity in GF reinforced HDPE. A very good retention of mechanical properties is observed.

Nanocyl can provide injection molding guidelines to get the best surface conductivity in combination with the best surface quality.
Multi-Layer Fuel Lines

• Conductive PA 12 (layer)

• Keeping PA 12 properties while being electrically conductive and protected from ESD

• Conductivity not sensitive to fuel contact, fl L, C, etc.

• Fits to current MLT technology of resin manufacturers

• Highly flexible

• Fits with standard extrusion equipments
Tube extrusion application: Conductive Tubing – Fuel lines

Surface resistivity of tubes after ageing in fuels and under several deformation constraints – PA12/NC7000 composites – External data SAE J 1681

- PA12/NC7000 based tubes present very good retention of SR under up to 100% of strain after 300h of ageing, this in different kind of fuels (Diesel and Fluid C but also Biodiesel, and FAMB)
- Flexibility of tubes remains within specification too

Nanocyl can provide tube extrusion guidelines to get the best surface conductivity in combination with the best surface quality
## Part 1: NC7000 Loading and Process Temperature

<table>
<thead>
<tr>
<th>Extruder Temperature (°C)</th>
<th>Surface Resistivity (Ohm)</th>
<th>Surface Aspect</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>7%wt CNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>10E4</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td>245</td>
<td>10E3</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td>260</td>
<td>10E3</td>
<td>Roughness – glossy</td>
</tr>
<tr>
<td><strong>4%wt CNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>10E5</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td>245</td>
<td>10E5</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td>260</td>
<td>10E4</td>
<td>Roughness – glossy</td>
</tr>
<tr>
<td><strong>2.5%wt CNT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>10E7</td>
<td>Small dots – glossy</td>
</tr>
<tr>
<td>245</td>
<td>10E5</td>
<td>Glossy</td>
</tr>
<tr>
<td>260</td>
<td>10E4</td>
<td>Glossy</td>
</tr>
</tbody>
</table>

Increase of process temperature increases strongly the conductivity of the tube, but surface keeps a certain roughness at most temperatures.
Part 2 : Additives

<table>
<thead>
<tr>
<th>Extruder Temperature (°C)</th>
<th>Surface Resistivity (Ohm)</th>
<th>Surface aspect</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% wt CNT No additive</td>
<td>245 10^4</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td></td>
<td>260 10^4</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td>4% wt CNT Additive A</td>
<td>245 10^4</td>
<td>Smooth – mat</td>
</tr>
<tr>
<td></td>
<td>260 10^4</td>
<td>Smooth – glossy</td>
</tr>
<tr>
<td>4% wt CNT Additive B</td>
<td>245 10^4</td>
<td>Roughness – mat</td>
</tr>
<tr>
<td></td>
<td>260 10^4</td>
<td>Smooth – glossy</td>
</tr>
</tbody>
</table>

Additives help to obtain a better surface aspect.
Conductive Resins for Body Panels & Windshields (injection & extrusion)

- E-paintable
- Superior HDT resistance
- Class A surface
- Weight reduction
- No color matching
Non ESD applications for Automotive
Conductive Resins for Automotive Heating Seats materials

- Extrusion of thermoplastics (ABS)
- 2K molding panel (TPU, PVC)
- Coating over textile fabrics (PU)

Technical specifications

- SR < 10 ohm/sq
- Soft finishing
- 12 V adaptable
Temperature control through voltage

Heating systems
Heating systems

High stability and homogeneity

Evolution of the temperature for 6 cycles (5 min on, 5 min off)

- Thermomètre
- Thermocouple

Graph showing temperature over time.
Strong influence of NC7000 on G1C

Fracture toughness: Bridging of the micro-cracks

Fig 9. TEM micrograph of a multi-wall carbon nanotube bridging a matrix crack.

Fig 10. SEM micrograph of a DWCNT/epoxy composite. A surface crack, induced by etching, is bridged by the nanotubes.
On industrial level, Sizicyl did improve Compression strength by 7-10 % compared to reference material.

Today, application are fishing rods, formula 1

Compression after Impact is improved by 40 % thanks to localization of NC7000 at the fiber interface.
Lithium batteries: Performance improvement by CNT - particles bonding mechanism

Source: High-density positive electrodes containing carbon nanotubes for use in Li-ion cells, Kyuyun Sheem, Young Hee Lee, Hong S. Lim, Journal of Power Sources 158 (2006) 1425-1430
Lithium batteries: Benefits brought by CNTs

- Improve conductivity of the electrode
- Improve number cycles / reduce capacity loss
- Improve power density
- Reduce battery temperature

**Benefits brought by CNTs**

- **LiFePO₄ cathode**
  - Discharge capacity (%)
  - Power density (W/kg)
  - Improve conductivity of the electrode
  - Improve number cycles / reduce capacity loss
  - Improve power density
  - Reduce battery temperature
Sensors

Temperature sensors

Gas/liquid sensors