Arkema Graphistrength® Multi-Walled Carbon Nanotubes

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ABSTRACT

Arkema Inc. produces multi-walled carbon nanotubes (CNT's) under the trade name *Graphistrength®*. Typical dimensions are 10-15 nm in diameter (5-15 walls) and 1-10 microns in length. Commercial and developmental products comprise plain CNT's (*Graphistrength®* C100), high-purity CNT's (*Graphistrength®* U100), thermoplastic masterbatches, water dispersions and epoxy pre-mix. Masterbatches, which comprise CNT's blended in a resin (up to 50%) have advantages – CNT's in a resin are easier to handle and dispersed already. Shown is the value of the masterbatch approach. Electrical conductivity data are presented for a variety of polymers containing CNT's – polyamides, polycarbonate, polyesters, and fluoropolymers. Mechanical properties data are presented as well. For epoxy, use of a masterbatch enables properties above that possible with plain CNT's – and simultaneous increase in both strength and toughness – an excellent combination.

Keywords: multi-walled carbon nanotube, masterbatch, Arkema, Graphistrength, composite

1 INTRODUCTION

Carbon nanotubes (CNT's) are subject of enormous interest world-wide – based on extraordinary properties:

- electrical – conductivity to 10^5 $ohm^{-1}cm^{-1}$
- mechanical – tensile modulus approximately 1,000 GPa
- thermal – conductivity approximately 3,000 watts/meter-K (exceeds diamond)

The general structure of a CNT is depicted in Figure 1. It can be regarded as a rolled graphene sheet. There are three types – single-walled, double-walled, and multi-walled. Double- and multi-walled systems comprise tubes concentrically nested – depicted in Figure 2. Electrical properties depend on the angle at which graphene sheet is rolled. See Figure 3. *Zig-zag* and *chiral* structures are semiconductive. *Arm-chair* structure is metallic. [1] Because of larger diameters, and thus more graphite-like structure, this construct does not apply to multi-walled carbon nanotubes, which are metallic. [2]

CNT's have been discovered in Middle Ages artifacts – the legendary *Damascus swords*. [3] However, not until the early 1990's was there structure elucidation and recognition as a distinct allotrope of carbon. [4,5,6]

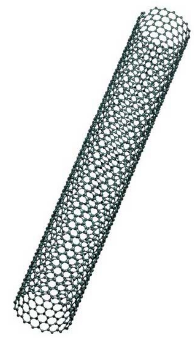

Figure 1. Structure of Single-Walled Carbon Nanotube

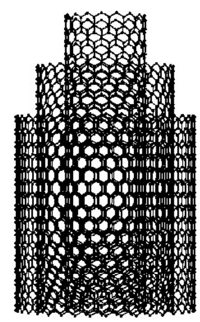

Figure 2. Depiction of Nesting of Tubes in a Multi-Walled Carbon Nanotube

One area of interest in CNT's is incorporating them into a polymer to produce a composite having enhanced properties, specifically:

- Improved electrical conductivity. This is at incorporation levels far below that needed with other conductive fillers, such as carbon black or metal powders. Said lower levels enable preservation of other polymer properties, such as strength, permeability, cost, etc. End-use applications include coatings for electromagnetic shielding, composites for automotive fuel systems, and composites amenable to electrostatic painting.
- Improved mechanical properties. This is primarily for thermosets like epoxies and polyesters. End-use

applications include aeronautical products and sporting goods.

In addition to improved electrical and mechanical properties, recent studies have shown exceptional performance in flame retardancy – at CNT concentrations ≤ 0.5%. [7]

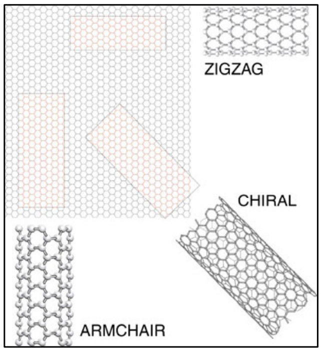

Figure 3. Depiction of Rolling of a Graphene Sheet

2 GRAPHISTRENGTH® PRODUCTS

Arkema Inc. manufactures multi-walled CNT's at Lacq, France. Process is chemical vapor deposition at elevated temperature of ethylene on metal/ceramic catalyst. Arkema CNT's and CNT-containing products are trademarked *Graphistrength®*.

SEM and TEM images of plain CNT's, i.e., Graphistrength C100, are presented in Figure 4. CNT's exist in bundles – median diameter approximately 10-20 microns. Diameter of individual CNT's is approximately 10-15 nanometers – corresponding to approximately 5-15 concentric tubes, with lengths approximately 1-10 microns.

As shown, multi-walled CNT's exist in bundles. A key point concerns how to prepare said CNT's for best use. Improving electrical conductivity is a crucial area. Electrical conductivity in a composite containing CNT's relies on percolation, as it does with other conductive fillers. Percolation is the state at which conductive filler particles interconnect to form a continuous network in which there can be current flow.

If bundles are not dispersed in composite at all, there would be low electrical conductivity – as all are surrounded by insulating polymer. Likewise if all CNT's are removed from bundles and perfectly dispersed, there would be low electrical conductivity – as all CNT's are surrounded by insulating polymer. [8] Needed is dispersion that enables percolation, i.e., connections of CNT's. Perfect dispersion is not needed, but rather that in which CNT layers and seams can connect throughout.

To this end, Arkema offers masterbatch products, in addition to plain CNT's. Masterbatches are composites comprising CNT's already introduced into a resin. Benefits are:

- easier handling – density of approximately 1 g/cc, versus approximately 0.1 g/cc for plain CNT's
- good dispersion established already

There are two types of masterbatches:

- specific – CNT's in a resin (e.g., polyamide-6) matching end-use polymer
- general – CNT's in a general-purpose resin

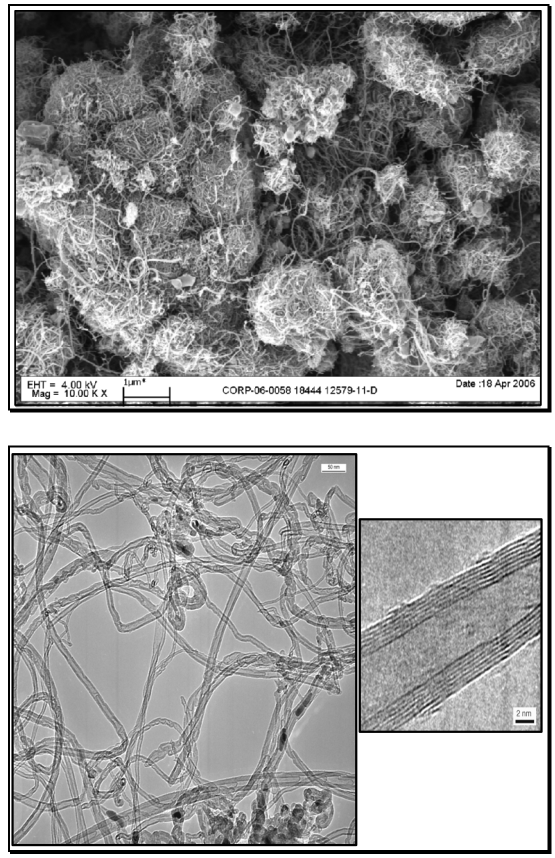

Figure 4. Graphistrength C100 Images - SEM (upper) and TEM (lower)

Current Graphistrength products are:

- *CNT's*
  - C100 plain carbon nanotubes (>90%)
  - U100 high-purity plain carbon nanotubes (> 97%)
- *Specific Masterbatches*
  - CM1-20 20% CNT, 80% polyamide-12
  - CM3-20 20% CNT, 80% polyamide-11
  - CM6-20 20% CNT, 80% polyamide-6
  - CS1-015 1.5% CNT, 98.5% epoxy (diglycidyl ether bisphenol A)
- *General Masterbatches*
  - 200 P50 50% CNT, 50% block copolymer
  - CM12-25 25% CNT, 75% general-purpose resin (developmental)

3 EXPERIMENTAL

Production of CNT-containing thermoplastic composites was with a DSM Research B.V. MIDI 2000 twin-screw extruder. Production of CNT-containing epoxies employed only stirring/shaking. Electrical conductivity was by 2-probe on freshly-fractured ends coated by silver paint. Mechanical properties were measured with a Zwick/Roell Z005. SEM imaging was with a Gemini LEO 1530, and optical imaging with a Nikon Eclipse ME 600.

4 PERFORMANCE

Consider the utility of the general masterbatch – Graphistrength CM12-25. In Figure 5 is shown the electrical conductivity of several composites comprising 2% CNT's. CNT's were introduced plain, and in CM12-25, by melt mixing. Performance with CM12-25 is as good or better than achievable with plain CNT's. This highlights general utility, especially considering that masterbatch is easier to use.

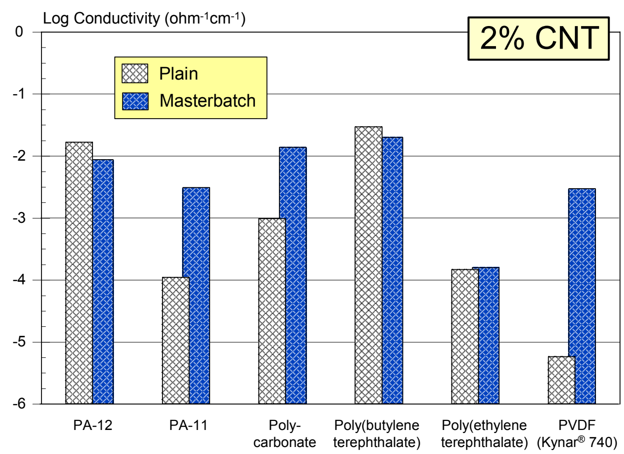

Figure 5. Electrical Conductivity of CNT-Containing Composites. Concentration of CNT's is 2% by weight. Masterbatch is CM12-25.

Performance in polycarbonate was examined in greater detail. In Figure 6 is shown electrical conductivity as a function of CNT concentration. CNT's were introduced plain, and in CM12-25. Note that CM12-25 provides for better conductivity, and a lower percolation level.

Mechanical performance in polyamide-11 was examined. See Figure 7. Tensile modulus increases and elongation-at-break decreases with increasing CNT concentration. CNT's were introduced in CM12-25.

Mechanical performance in epoxy was examined. See Figure 8. Flexural modulus data were compared for two systems comprising 0.5% CNT's. CNT's were introduced plain and in CM12-25. Note the system incorporating

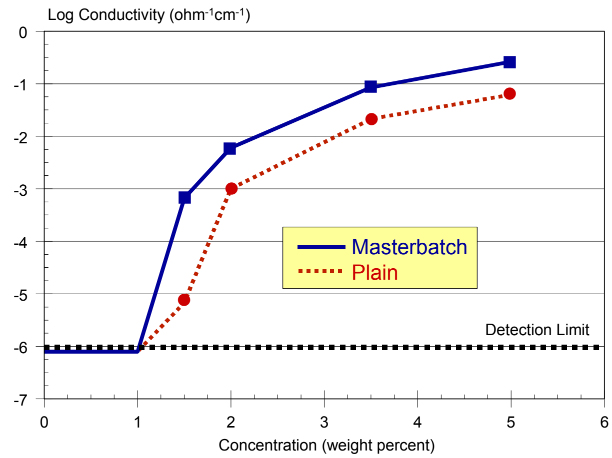

Figure 6. Electrical Conductivity of CNT-Containing Polycarbonate Composites. Masterbatch is CM12-25.

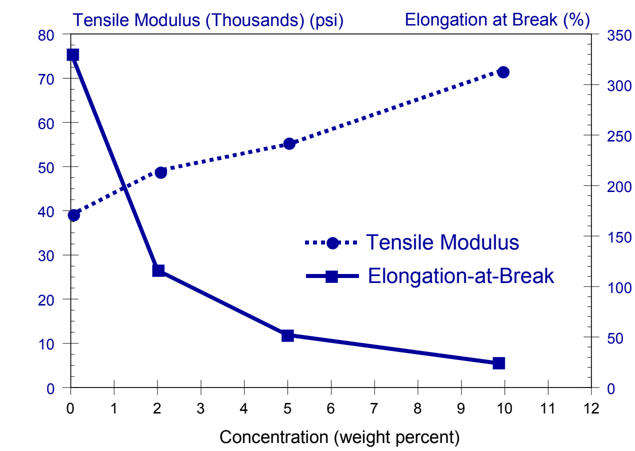

Figure 7. Mechanical Properties of CNT-Containing Polyamide-11 Composites. CNT's introduced in CM12-25

CM12-25 not only has improved strength (i.e., higher flexural modulus), but substantially increased toughness. This is a very desirable combination. Possibly interaction of CNT's with epoxy matrix transfers load to CNT's, resulting in improved modulus, and well-dispersed CNT's serve as crack stoppers, resulting in improved toughness. [9]

5 SUMMARY

Arkema produces multi-walled carbon nanotubes – plain and in masterbatches. Masterbatch products have advantages – easy handling and good performance in a wide range of polymers. Moreover in epoxy, materbatch product enables increase in strength and toughness – a very desirable combination.

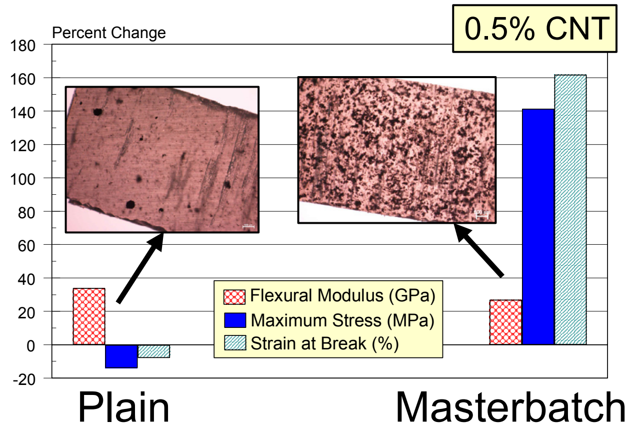

Figure 8. Mechanical Properties and Transmission Optical Images of CNT-Containing Epoxy Composites. Concentration of CNT's is 0.5% by weight. Data are plotted as change versus plain epoxy (Flexural Modulus = 2,950 MPa, Maximum Stress = 41.9 MPa, Strain-at-Break = 1.3%). Magnification of photographs is 15X. Epoxy is diglycidyl ether of bisphenol A and dicyandiamide.

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