Composites with Multi-Walled Carbon Nanotubes

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ABSTRACT

Multi-walled carbon nanotubes are of great interest – primarily based upon their electrical and mechanical properties. The main application is in polymer composites – where at low concentrations they provide substantial improvements in electrical and mechanical performance. They also are very effective pigments and UV stabilizers. Discussed is the performance of thermoplastic, thermoset, and elastomer composites comprising Arkema Graphistrength® multi-walled carbon nanotube products, with emphasis on the utility of masterbatches.

Keywords: Arkema, composite, conductivity, masterbatch, nanotube

1 INTRODUCTION

Carbon nanotubes are the subject of great interest, based upon their properties:

- electrical conductivity to 10^5 $ohm^{-1}cm^{-1}$
- mechanical tensile modulus ca. 1,000 GPa
- thermal conductivity ca. 3,000 W/m-K (> diamond)
- pigmenting ca. 40-fold > carbon black
- UV stabilization ca. 50-fold > carbon black

The structure of a carbon nanotube can be regarded as a rolled graphene sheet. [1-6] The major types are single-walled and multi-walled. Multi-walled carbon nanotubes comprise concentric tubes. See **Figure 1**.

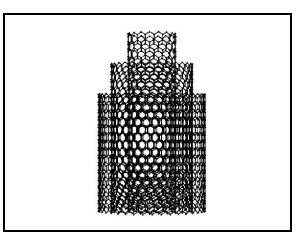

Figure 1. Structure of a multi-walled carbon nanotube

2 APPLICATIONS

The most important application of multi-walled carbon nanotubes (*hereafter called CNT's*) is in polymer composites – incorporating them into a polymer to enhance properties:

- electrical conductivity. This is achieved at concentrations lower than that needed with other conductive additives, such as carbon black. See **Figure 2**. [7] These lower concentrations enable preservation of polymer properties, such as strength. Applications include electrostatically dissipative electronic components.
- mechanical properties. This is primarily for thermosets. Applications include vehicular components and sporting goods.
- color. At low concentrations, pigmenting is excellent. Applications include coatings.
- UV stability. At low concentrations, resistance to UV degradation is greatly enhanced. Applications include composites for outdoor use.
- flame retardancy. Studies at the National Institute of Standards and Technology have shown excellent performance in flame retardancy – at CNT concentrations ≤ 0.5% (by weight). [8]

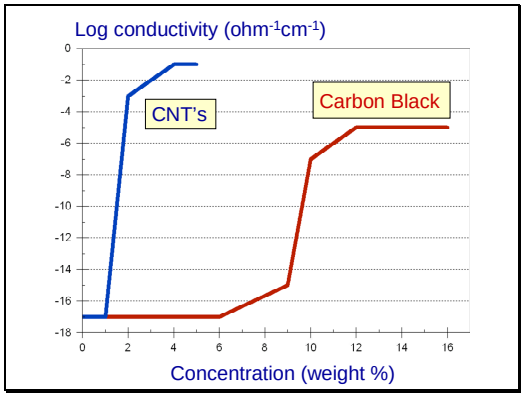

Figure 2. Percolation in a composite with CNT's and carbon black. Constructed from data in [7].

3 ARKEMA PRODUCTS

In 2011, Arkema commissioned a 900,000 lbs/year plant for CNT's in Mont, France. The process is catalytic chemical vapor deposition at elevated temperature of ethylene on a metal catalyst supported on a metal oxide. Arkema CNT's and CNT-containing products are sold

under the *Graphistrength*® name. Arkema CNT's are renewable – all ethylene is from bio-ethanol.

SEM and TEM images of CNT's (Graphistrength® C100) are shown in **Figure 3**. CNT's exist in agglomerates with a median diameter of ca. 400 microns. The diameter of individual CNT's is 10-15 nanometers, which corresponds to 5-15 concentric tubes (average ca. 7). The lengths of CNT's are 0.1-10 microns.

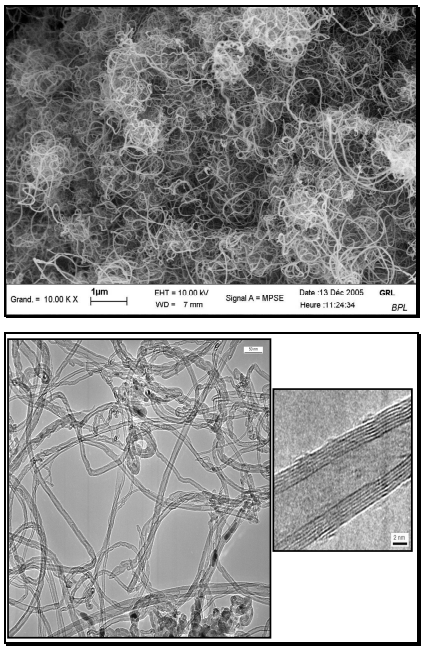

Figure 3. Graphistrength® C100. SEM (upper) and TEM (lower)

Critical for any application is proper dispersion of CNT's in the polymer composite. To this end, Arkema offers a wide variety of standard and custom-made masterbatch products. Masterbatch products are pre-mixes of CNT's in a polymer. Benefits are:

- good dispersion
- easy handling – density approximately 1 g/cc, versus approximately 0.1 g/cc for plain CNT's

4 RESULTS AND DISCUSSION

4.1 Thermoplastics

Consider the general-purpose masterbatch – Graphistrength® CM12-30 (30% CNT's in cyclic butylene terephthalate). **Figure 4** shows the electrical conductivity of several composites comprising 2% CNT's. CNT's were introduced as Graphistrength® C100 (plain CNT's), or as CM12-30, both by melt mixing. Performance with CM12-30 is as good or better than that obtained with plain CNT's. This highlights masterbatch utility, especially since a masterbatch is easier to use.

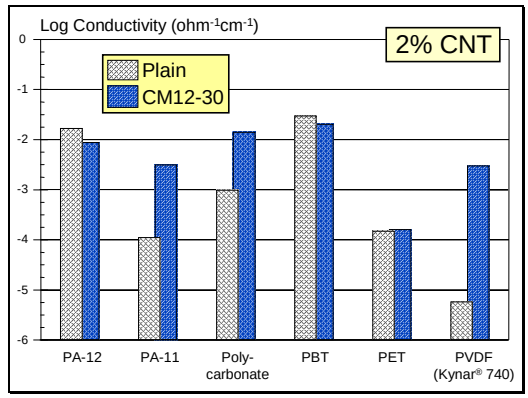

Figure 4. Electrical conductivity of CNT-containing composites. Concentration of CNT's is 2% (by weight).

Performance in polycarbonate was examined in more detail. **Figure 5** shows electrical conductivity as a function of CNT concentration. CNT's were introduced as plain CNT's, or as CM12-30, both by melt mixing. Note that CM12-30 provides for a much lower percolation level.

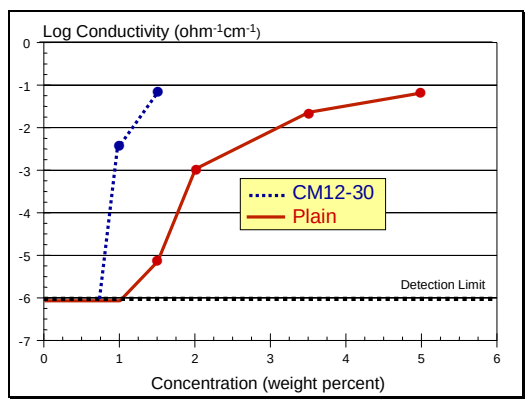

Figure 5. Electrical conductivity of CNT-containing polycarbonate composites

Mechanical performance of polypropylene composites was examined. See **Table 1**. CNT's were introduced as Graphistrength® CM14-25 (25% CNT's in polypropylene). Note the substantial improvement compared to polypropylene without CNT's.

4.2 Thermosets

Figure 6 shows the improvements in mechanical properties that result in a carbon-fiber-reinforced epoxy composite containing only 1% CNT's – introduced as

Graphistrength® CS1-25 (25% CNT's in bisphenol-A epoxy). Improvement is achieved with no effect on Tg.

Table 1. Increase in mechanical properties of polypropylene containing 0.5% CNT's (by weight) versus polypropylene without CNT's

	Increase
Impact Resistance (kJ/m^2)	**15 %** (5.3 → 6.1)
Tensile Modulus (MPa)	**16 %** (1,226 → 1,446)
Flexural Modulus (MPa)	**21 %** (967 → 1,174)
Elongation-at-Break (%)	**11 %** (555 → 615)

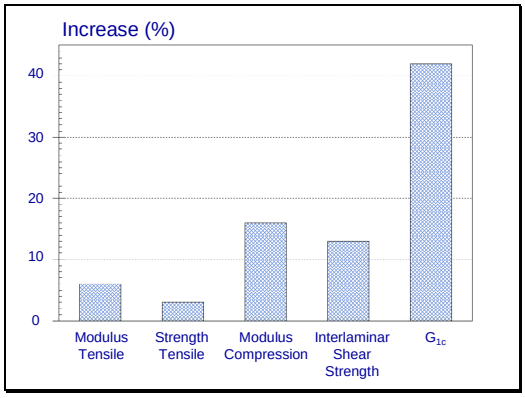

Figure 6. Mechanical properties of CNT-containing carbon-fiber-reinforced epoxy composite (50% fiber). Shown is relative improvement with 1% CNT's (by weight). G_{1c} is a measure of resistance to fracture.

Work at Texas A&M University has also shown the value of CNT's in epoxy composites – introduced as plain CNT's (Graphistrength® C100). [9] See **Figure 7**. Toughness is improved with only 1% CNT's. Note the substantially larger area under curve for composite with CNT's.

4.3 Elastomers

Figure 8 shows the improvements in electrical performance achieved with CNT's in elastomers. Note the low amount of CNT's needed versus carbon black, and the maintenance of mechanical properties. CNT's were introduced as Graphistrength® CE2-40 (40% CNT's in nitrile rubber).

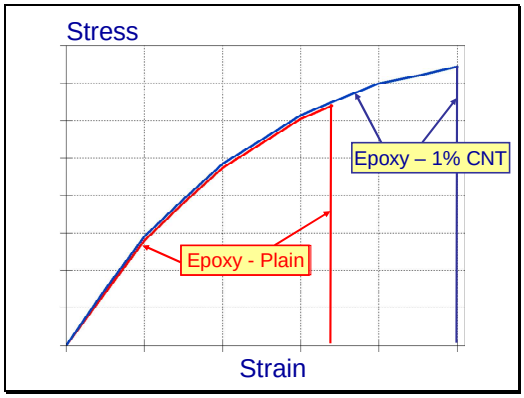

Figure 7. Mechanical properties of CNT-containing epoxy composite. Concentration of CNT's is 1% (by weight). Constructed from data in [9].

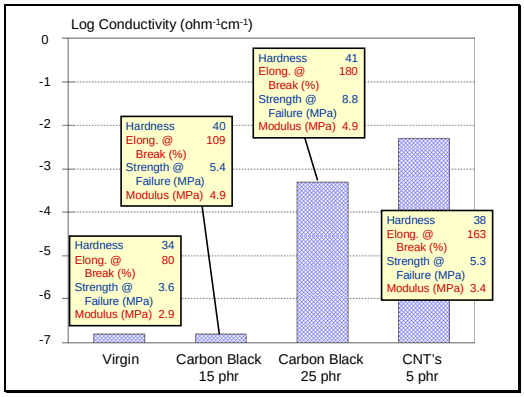

Figure 8. Electrical and mechanical properties of CNT-containing nitrile elastomer composites

Work at Designed Nanotubes, LLC, has also shown the value of CNT's in elastomers. [10] Using surface treated CNT's, substantial improvements are made in performance – notably abrasion resistance. See **Table 2.**

Table 2. Select mechanical properties of CNT-containing elastomer composites. Concentration of CNT's is in weight percent. Data reproduced from [10].

	0%	**1.5%**
Cure Time (min)	4.49	3.35
Shore A	63	67
Tensile Srength (psi)	2,429	2,640
Tensile Elongation (%)	435	381
Modulus (psi)	352	501
Tear Stength (ft-lbs/in)	279	324
Taber Abrasion (g) (100 g, 100 cycles)	0.119	0.053

4.4 Pigmenting and UV Stabilization

CNT's show excellent performance in pigmenting composites – ca. 40-fold better than carbon black. See **Figure 9** for polyethylene. CNT's were introduced as Graphistrength® CM4-30 (30% CNT's in polyethylene).

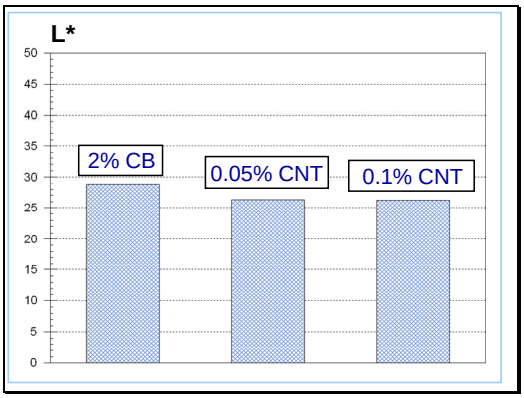

Figure 9. Black-scale of polyethylene composites containing CNT's and carbon black.

CNT's show excellent performance in improving UV resistance of composites – ca. 50-fold better than carbon black. See **Figure 10** for polyethylene. CNT's were introduced as Graphistrength® CM4-30 (30% CNT's in polyethylene).

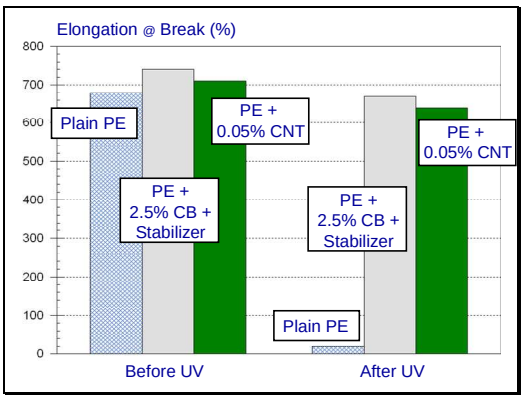

Figure 10. UV stability of polyethylene composites containing CNT's and carbon black. 800 hours Xenon exposure.

4.5 Concrete

Even concrete mechanical properties are improved with the use of CNT's. [11] See **Figure 11.** CNT's were introduced as Graphistrength® CW2-45 (45% CNT in Na-carboxymethylcellulose).

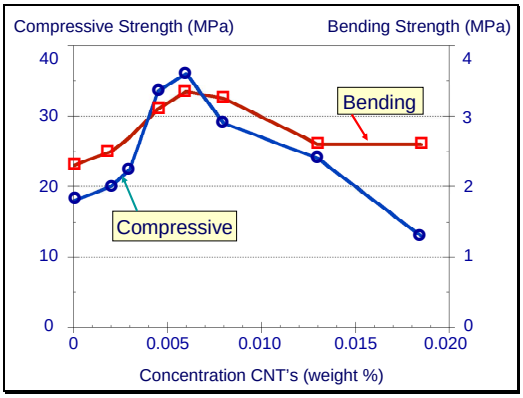

Figure 11. Improvement in mechanical properties of CNT-containing concrete. Constructed from data in [11].

5 CONCLUSIONS

CNT's show excellent performance in improving the performance of composites: thermoplastics, thermosets, elastomers, and even concrete. They do this at low concentrations (<5% by weight). Performance can be maximized, and handling made most convenient, through the use of masterbatches.

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