

# INDUSTRIAL PRODUCTION AND APPLICATIONS OF CARBON NANOTUBES

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## SUMMARY

Carbon nanotubes were discovered in the early 90's and many research groups (academia or start-up mainly) have demonstrated the potential of these new materials.

Recently, major chemical companies have launched projects around carbon nanotubes. Among them, Arkema has started to develop the Graphistrength™ multi-wall carbon nanotubes with a first large-scale laboratory pilot having a capacity of 10 tons/yr that started in February 2006.

The purpose of these projects is to develop industrial processes (both in term of the productivity and the consistency of the production) to introduce CNT in large scales applications.

Such applications can be found in the fields of aeronautics, automotive, electronics, and many others, where the incredible performances of CNT as far as electrical conduction or mechanical improvements for example could be used to develop new light materials with improved properties.

The development of CNT in such applications will also necessarily be linked to the development of reliable processes to introduce these materials in the final industrial parts.

## INTRODUCTION

Carbon Nanotubes (CNT) were discovered in the 1990s following the discovery of fullerenes [1]. CNT consist of graphitic sheets, which have been rolled up into a cylindrical shape.

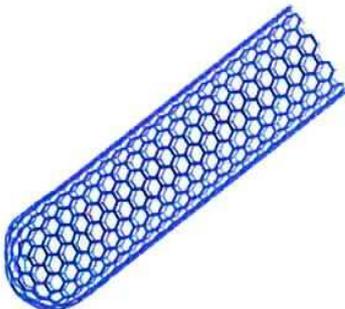


Figure 1: Single Wall Nanotube

Depending on the synthesis process, the length of CNT is in the range of micrometers with diameters smaller than 100 nm, and usually closer to 10 nm.

Furthermore, there is not just a single kind of CNT, but various ones depending on the number of tubes (Single Wall Nanotubes - SWNT, Double Wall Nanotubes - DWNT, Multi Wall Nanotubes MWNT), on the arrangement of the hexagon rings along the tubular surface (CNT can be metallic or semi conducting), or on the purity of the CNT produced. Figure 1 shows a picture of a SWNT and Figure 2 of a MWNT.

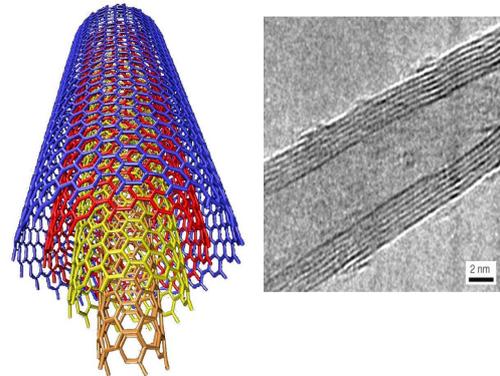


Figure 2: Multi Wall Nanotube

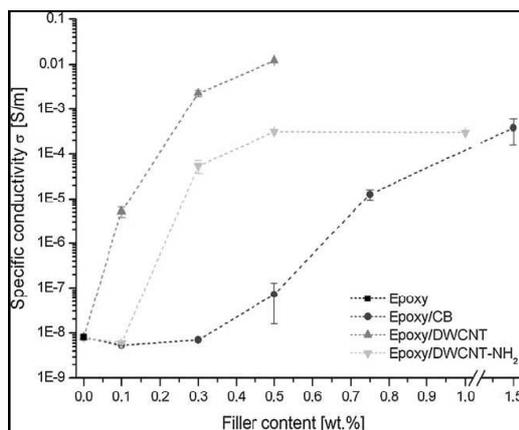
CNT have extraordinary mechanical, electrical or thermal properties in the pure state [2-4].

Material	SWNT	MWNT	Steel
Young's modulus (GPa)	1054	1200	208
Tensile Strength (GPa)	150	150	0,4
Density (g/cm <sup>3</sup> )		2,6	7,8
Thermal Conductivity W/m.K	3000		
Electrical Conductivity S/m	10 <sup>5</sup> - 10 <sup>7</sup>		

Table 1: Physical properties of Carbon Nanotubes

Thanks to their high aspect ratio and, hence, the low percolation threshold that can be achieved, they can also be used as modifiers in various systems to impart extremely promising properties for applications particularly in materials science.

It has been shown that, once a good dispersion of CNT is achieved, it is possible to reach the electrical conductivity or to improve the mechanical properties of thermoset resins and composites at loadings even below 1% as illustrated in Figure 3 [5].



**Figure 3: Conductivity vs. filler content [5]**

The initial work was primarily performed by academics or at start-ups. Although very interesting and insightful studies were made, this path left important limitations as far as the industrial developments of these nanotechnologies were concerned.

Among other major chemical companies, Arkema (18 000 employees, 5.7 G€) has launched the development of multi-wall carbon nanotubes under the brand name Graphistrength™ to finally make nanotechnologies an industrial reality.

## INDUSTRIALIZATION OF NANOTECHNOLOGIES

Because of the very limited production available until now, not only were the prices of the CNT available extremely high, making their remarkable efficiency much less attractive on a performance/price point of view, but the scale of the tests that could be performed for more advanced qualification programs was also quite limited.

Because the process conditions for making the CNT were not always as controlled as can be required, there were even variations in the properties of the products developed by a single "supplier": this obstacle was making the development of industrial applications a challenge as long as the consistency of the production was not settled.

In the beginning of this decade, major chemical corporations all over the world have also begun to be involved in the development of projects around CNT.

For Arkema, as a major industrial player, the focus was in particular to be able to develop a process that could be easily up-scaled in order to consistently produce a quantity of material adapted to tackle large volumes markets. This would produce CNT at a price "low" enough to make this new nano-technology a valid approach on a price/performance basis for creating innovative materials.

A major step in that direction was taken at the beginning of 2006 with the start of a first large-scale laboratory pilot having a capacity of 10 tons per year. This unit is dedicated to the synthesis of multi-wall carbon nanotubes at high productivity

(Graphistrength™) and is only the first step of a larger industrial project.

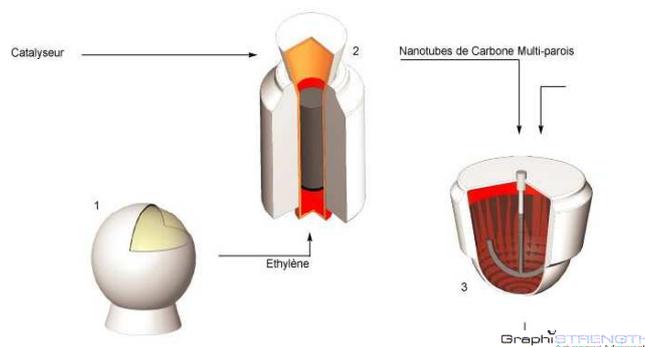
## 1. SYNTHESIS

Among the various forms of CNT that may exist, the scale-up of MWNT production was identified as the best path towards industrialization.

First, the reaction leading to MWNT was the one leading to the highest yield in term of purity of the product. By contrast, during the synthesis of SWNT, a lot of amorphous carbon is produced that needs further purification. As stated in [6], the mass unit for the sales of SWNT is the gram. Major players have developed their own catalytic systems for the production of MWNT that ensure a high yield in terms of production per gram of catalyst.

Even if the precise details of the synthesis process are proprietary, Arkema's process can be illustrated in Figure 4:

1. A gas (for example Ethylene) is used as a carbon feedstock. The catalytic source is derived from Fe.
2. The synthesis is carried out at high temperature using a fluidized bed.
3. MWNT bundles are obtained and formulated in order to provide them with optimized properties.



**Figure 4: Scheme of the synthesis process**

Fluidized bed processes are very well known in the polymer industry and scaling-up of such processes is something Arkema's engineers master.

A lot of dedication and time has been directed towards the development of a highly reproducible process in order to provide very consistent materials. It is particularly important to have a very accurate control of the process parameters such as the synthesis temperature. The synthesis parameters are the key factor in controlling the structure of the tube.

The definition of an efficient catalyst has also been a huge point in the development of the project.

Once these parameters were and the scale-up designed, Arkema started a large-scale laboratory pilot with a capacity of 10 tons

per year of MWT under the trade name Graphistrength™ in February 2006 in Lacq, France (Figure 5).

Graphistrength™ MWNT have from 10 to 15 walls with an outer mean diameter around 12 nm with an apparent density in the 50 to 150 kg/m<sup>3</sup> range.



Figure 5: Arkema Laboratory Pilot in Lacq

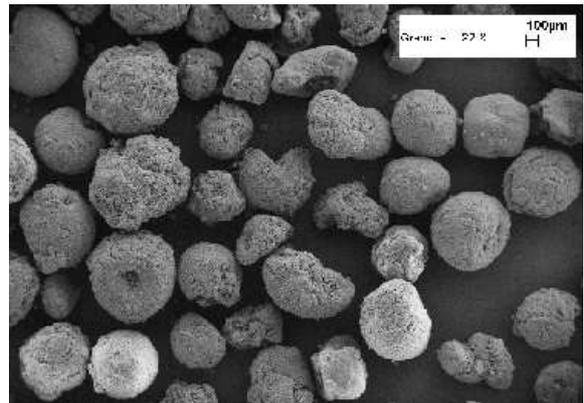
## 2. GRAPHISTRENGTH™ DISPERSION

Even if MWNT are indeed a nanotechnology, they are produced in powder form as highly entangled MWNT bundles. The bundles have a size of several hundred of micrometers as illustrated in Figure 6.

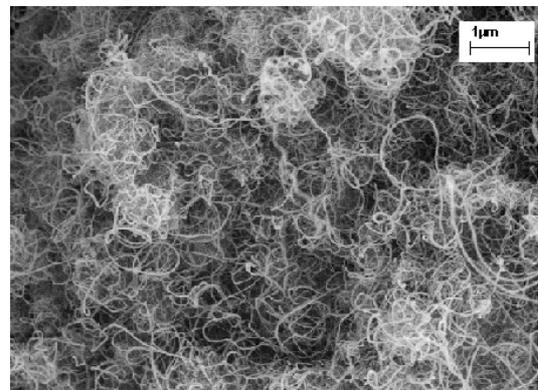
Although this product form presents many advantages, in particular concerning the handling (the powder is free falling with an easy dosage), one of the main challenges in order to obtain the optimal properties of CNT is the dispersion of CNT.

As a matter of fact, the ultimate goal when using Graphistrength™ in any given application is to go from the initial bundle state to dispersion where any single nanotube is dispersed in the matrix.

Thus, the percolation threshold (percentage at which CNT exhibits their optimal properties) will not only depend on the properties of the CNT, but also on the process that is used to disperse them and on the affinity between the CNT and the matrix in which they are dispersed.



a/



b/

Figure 6: SEM images of MWNT bundles (a: global image and b: close-up of the surface of the embedded powder)

In order to improve the dispersion of CNT, it is possible to play on modifications of the CNT surface through physical or chemical modifications of the surface of the nanotubes.

Chemical modifications [7] have been widely studied. One of the drawbacks of these approaches from an industrial standpoint is that these chemical modifications are often carried out at a very low content of CNT in very dispersed media (generating a lot of Volatile Organic Content (VOC) to deal with). These modifications also have the drawback to attack the surface of the carbon nanotubes, often reducing their mechanical properties.

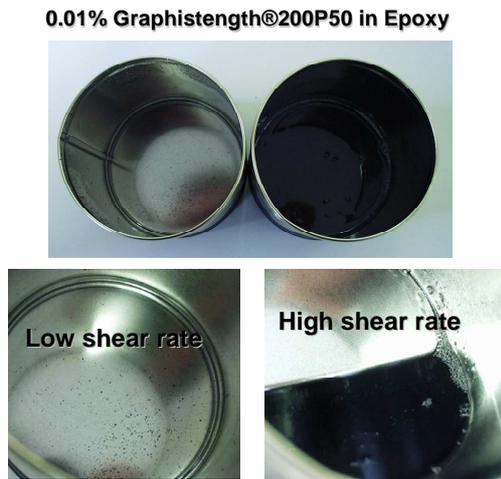
For physical modifications of the surface of the nanotubes, Arkema has developed a proprietary technique to produce products with high contents of carbon nanotubes without having to go through a process generating lots of VOC.

Arkema has also developed know-how and technologies to achieve a good dispersion of Graphistrength™. In order to disperse the carbon nanotubes in any matrix, high shear processes will have to be used. For thermoset resins, these processes may include ultra-sonic dispersion, or high shear devices. One illustration of the influence of the process is

illustrated in Figure 7, where an epoxy resin is modified with 0.005% of CNT (0.01% of Graphistrength 200P50):

On the left side, the modification is made with a low shear rate process: the dispersion is poor.

On the right side, the modification is made with a high shear rate process adapted to thermoset system: the dispersion is very good.



**Figure 7: Dispersion of Graphistrength® in epoxy**

One possible drawback of these processes is that they could lead to a length reduction of the nanotubes (hence a reduction of the L/D ratio and thus of their efficiency to modify the material properties). But, without such processes, it is very difficult to disperse the CNT bundles efficiently, especially without using high quantities of solvents. The conditions must therefore be carefully tailored to achieve the optimum trade-off.

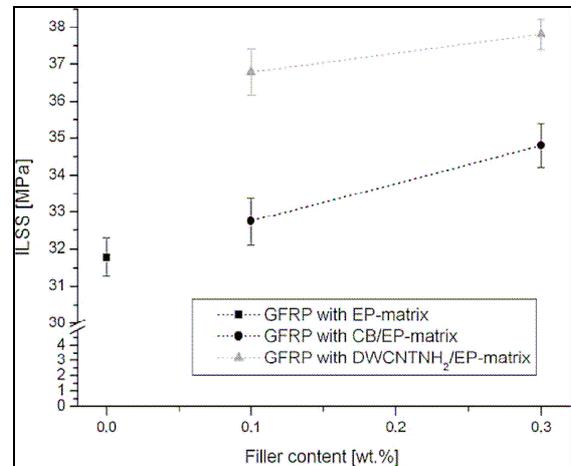
### 3. GRAPHISTRENGTH™ IN THERMOSET AND COMPOSITES: TOWARDS INDUSTRIAL APPLICATIONS

It appears that Graphistrength™ will be used in the composite aeronautic industry for two of the main properties they have: electrical conduction and improvement of the mechanical properties.

Because of the high aspect ratio (and the low percolation threshold), CNT can make a matrix conductive at very low levels [5], [16] to [19]. Depending upon the applicative requirements, the level of resistivity can be fine-tuned. A potential application in aeronautics is the production of a thermoset material that is conductive enough to evacuate the electrical charges that can accumulate within the parts.

The introduction of CNT in a matrix is also a way to improve the mechanical behavior of this matrix or the composite parts made with it. Examples are given in references [8] to [15].

Figure 8 from reference [10] illustrates the improvement in ILSS through the use of CNT.



**Figure 8: ILSS as a function of filler content [10]**

The points that still need to be worked out concern the processes in order to disperse and to use CNT.

As indicated above, due to the high Van der Waals forces existing between CNT, dispersed media were often used for introducing the CNT. If these tests were very insightful to learn about the potential of CNT ([17] to [19]), they are not really industrial as far as generating not only additional processing steps, but also a lot of VOCs. Avoiding the use of disperse media may well lead to a slightly less perfect dispersion of the CNT and to higher percolation thresholds (albeit always very small). Nonetheless, avoiding such techniques remains a *sine qua non* condition for industrialization.

The introduction of CNT usually leads to an increase in the viscosity. The better the Graphistrength™ are dispersed, the higher this increase is, as illustrated in Figure 9.

This rheology modification will be very important in the development of Graphistrength™ applications in aeronautics. For traditional composite processes, the amount of Graphistrength™ that can be introduced will be limited by the viscosity increase that may be tolerated. In example [10], RTM processes can be used with CNT modified epoxy resins but the amount of CNT introduced is limited to about 0.3%.

On the other hand, as this viscosity increase is particularly strong at low shear rates and lower temperature, it can be beneficial in processes such as filament winding.

This rheology modification can also be used as an advantage to develop innovative processes around well-know materials.

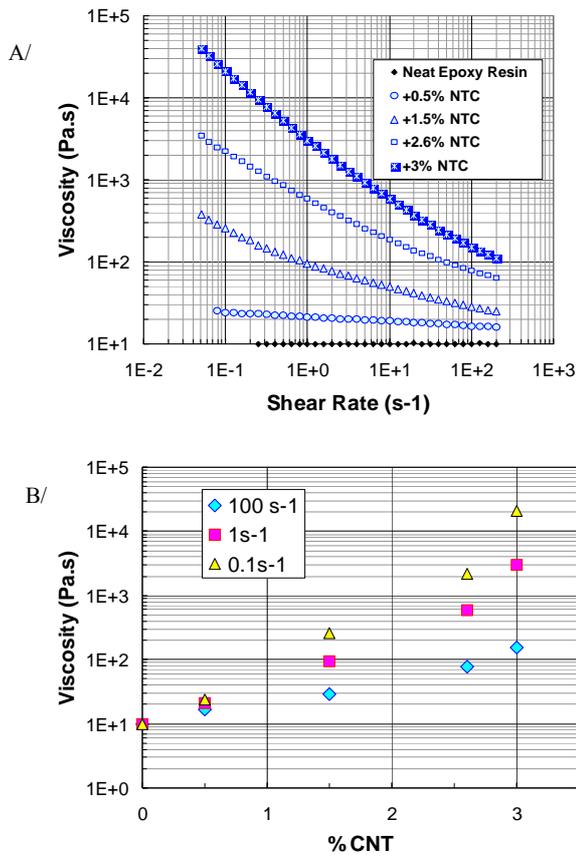


Figure 9: Example of rheology modification in LY5052 (Huntsman) with Graphistrength 200P50

#### 4. GRAPHISTRENGTH™ IN THERMOPLASTICS: TOWARDS INDUSTRIAL APPLICATIONS

Thermoplastics applications for Graphistrength™ will also be geared towards exploiting the exceptionally low percolation thresholds exhibited by these materials for electrical conductivity [20,21]. These values allow industrially useful resistivities to be reached at additive levels sufficiently below those of carbon black (CB) that better mechanical properties than for CB-based composites are expected. Typical target values are  $10^4$ - $10^6 \Omega \cdot \text{cm}$  for electrostatic dissipation, or  $10^6$ - $10^9 \Omega \cdot \text{cm}$  for antistatic applications. As shown in figure 10, such values are easily obtainable at only a fraction of the percentage of carbon black that would be required. Potential applications include automotive parts such as benders, where electro-spray painting is practiced; fuel lines, where electrostatic dissipation offers a crucial safety property.

In terms of mechanical reinforcement, CNT set themselves apart from carbon fibers by bringing strength in addition to modulus [22]. Heat treatments can modify polymer crystallinity, and hence mechanical properties [23]. For the closely related

carbon nanofibers, significant improvements have also been observed beyond thermoplastics, for elastomers [24].

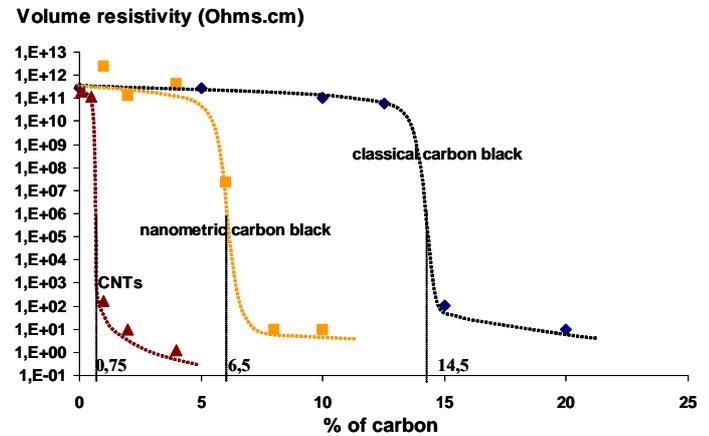


Figure 10: Volume resistivity as a function of carbon content for three carbonaceous materials in Kynar® PVDF

Just as was the case for thermosets, the correct dispersion of carbon nanotubes must be achieved to attain the additive's full potential. Dispersion in thermoplastics, however, is more difficult due to the high viscosity of molten polymers. Furthermore, the introduction of Graphistrength™ leads to an additional increase in the viscosity, as illustrated in Figure 11 [25]. This viscosity increase is again most strong at low shear rates, so high shear compounding is typically preferable.

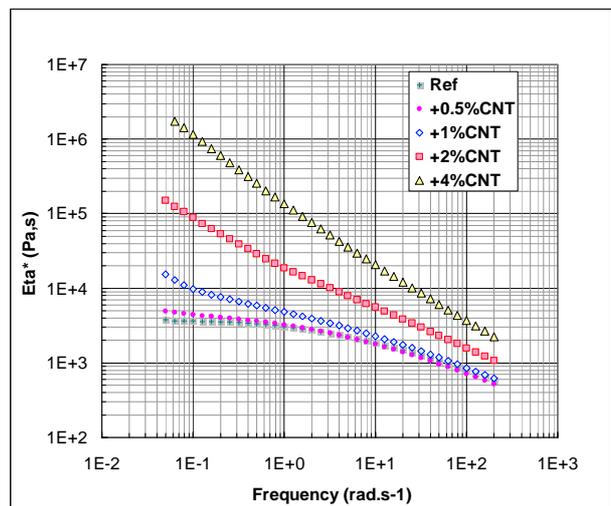


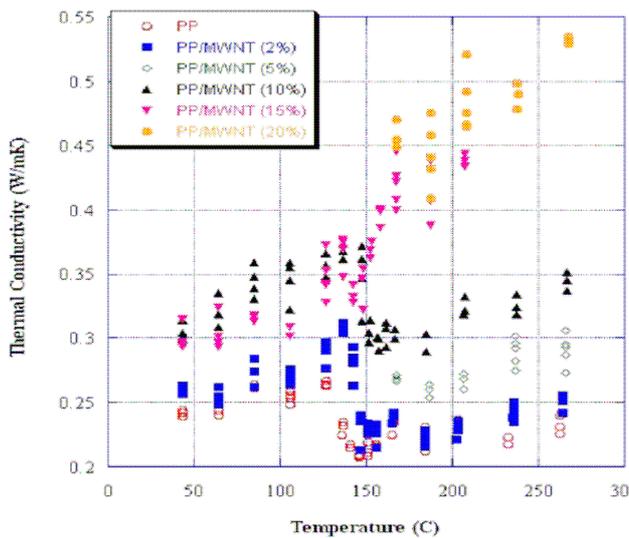
Figure 11: Evolution of complex melt viscosity versus frequency at 230 °C for different MWNT contents in Kynar® PVDF 720.

As for thermoset systems, this viscosity increase must be taken into account both during compounding and during subsequent transformation (injection, extrusion, etc.).

At this last step, alignment may or not occur, as discussed by Pötschke [25]. This can, in turn, lead to higher-than-expected percolation thresholds, but also to other, more beneficial, effects such as the best modulus increases [26].

In Arkema's experience the most rapid way to successful development is to first optimize the dispersion and transformation conditions, an area in which we are staking out the company's intellectual property.

Due to their high thermal conductivity, MWNT also enable the fabrication of composite materials with increased thermal conductivities. Figure 12 shows data at various temperatures for polypropylene/MWNT composites [27]: near room temperature, 15% MWNT result in >25% increases in thermal conductivity.



**Figure 12: Thermal conductivity of polypropylene with and without MWNT [27]**

## CONCLUSIONS

Arkema, as a major chemistry company, has launched an industrial project around Multi-wall Carbon Nanotubes under the brand name Graphistrength™ with a first large-scale laboratory pilot that started in February 2006.

Taking a lot of care in consistency and quality and with aiming towards a large production unit in the future, Arkema plans to develop applications in the aeronautic field where the properties of Graphistrength™ can be used.

To be successful, it will be particularly important to also develop consistent industrial processes to introduce the carbon nanotubes inside the final aeronautic parts.

This is an active area of research, and we are already proposing tailor-made solutions to our partners and customers.

## ACKNOWLEDGEMENTS

The authors would like to thank the other Arkema "nano"-people working on different aspects of the project.

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