# **USE OF CARBON NANOTUBES IN STRUCTURAL COMPOSITES**

Nadir Kchit, Michael Claes

Nanocyl SA, Rue de l'essor 4,5060 Sambreville, Belgium Email: nadir.kchit@nanocyl.com, Web Page: http://www.nanocyl.com

**Keywords:** Carbon nanotubes, carbon fiber reinforced polymer, thermoplastic

#### **Abstract**

Carbon nanotubes (CNTs) possess excellent intrinsic characteristics such as exceptionally high mechanical and conductive properties which make them the prime candidate to reinforce highperformance composite structures. However, location and dispersion state of the CNTs have particular importance to achieve the mechanical and electrical enhancement of carbon-reinforced composites. Different approaches to incorporate CNTs were investigated such as CNTs thermoplastic veils, CNTs thermoplastic powder doped prepreg, and CNTs adhesives. Each approach required specific dispersion solution to develop a large experience in incorporation of CNTs in different resins (thermoplastics, thermosets, etc.) using improved innovative mixing process, CNT surface modification (functionalization) or by adding dispersing agents or compatibilizers. The dispersion quality for each scenario was characterized before composite manufacturing. It was shown that the damage tolerance and electrical conductivity for multifunctional carbon fiber reinforced polymer were improved compared to conventional composite.

### **1. Introduction**

Since the first observation of CNTs in the early 1990s [1], huge improvements have been made in the understanding of this cutting-edge material. For a long time, carbon nanotubes were only categorized and used as "highly conductive fillers," but nowadays this nanotechnology is starting to exhibit its true potential and proves that it can improve or even impart new properties to polymers (mechanical, chemical, or thermal properties). At the end, the composite will not only offer electrical conductivity but will also present better mechanical or chemical or heat resistance under operation, which will allow researchers and engineers to develop, create, and design breakthrough materials and unprecedented technologies.

Nanocyl is one of the first companies established in Europe for the commercial supply of this family of novel material. From 2002, Nanocyl has built up its worldwide recognition by providing highquality products adapted to the customer's needs. Its expertise in tuning the carbon nanotubes properties and morphologies to obtain the best out of their intrinsic potential has made Nanocyl one of the most recognized producers of specialty carbon nanotubes and of materials and technologies using carbon nanotubes. Moreover, these knowledge and expertise have led Nanocyl to exploit further the CNT advantages by preparing concentrates, dispersions, and semi-formulated products out of various material families (thermoplastics, thermosets, elastomers, silicones, liquids, etc.).

Carbon fiber reinforced polymer is widely used in many applications such as aeronautic, wind turbines, vehicles and sport goods. Structural composites are subjected to fatigue loading which delamination is one of the most predominant and life-limiting failure mechanisms in composite structures. The growth of delamination is usually accompanied by a loss of composite stiffness which then quickly leads to final failure of the system. The method used to improve this property is the modification of the matrix by adding a toughening agent. Thermoplastic and rubbers are well known by their power to tougher the epoxy system [2-6]. Another approaches to toughen structural composite suggested in this paper are thermoplastic veils interleave and powder thermoplastic treated prepreg. The role of thermoplastic veils /powder incorporated between plies is to increase fiber bridging and toughen the interface fiber resin [7]. Thanks to the combination of good electrical and mechanical characteristic of CNTs and toughness of thermoplastic it is expected that the both damage tolerance and electrical conductivity will be improved

## **2. Materials and experiments.**

## **2.1 Carbon Nanotubes**

Numerous different carbon nanotubes can be produced by playing with carbon sources, catalyst, process, and temperature. At Nanocyl, large volumes of thin MWCNT (NC 7000™) are produced by catalytic chemical vapor decomposition Fig.1. A primary interest of NC 7000 is low percolation threshold for electrical conductivity toward other conventional carbon-based fillers. Nanocyl is also leading pro-actively health, safety, and environment matter all long the life cycle of product containing MWCNT NC 7000. Interaction with several key players and participation to different European projects has led to numerous data collection and positioning on hazard, exposure, use phase, and end of life. As a consequence, registration dossiers under REACH have been filed and provide information on the safe uses of MWCNT. Further, NC 7000 functionalized with amino groups (NH2-NC 7000) were produced by a patented plasma process. The amino groups should improve the dispersion of the CNTs into the matrix leading to an increase of mechanical performances and a lower percolation threshold for electrical conductivity.



**Figure 1.** Transmission electron microscopy of multiwalled carbon nanotube NC 7000™

# **2.2 Carbon Nanotube-Doped Thermoplastics**

Nanocyl's expertise for the dispersion of CNTs in thermoplastics is used to produce high value masterbatches or compounds (PLASTICYL™ grades). Plasticyl products provide easy to use masterbatches containing CNT already pre-dispersed. In some cases, for equal surface resistivity, a reduction up to 25 % of CNTs loading could be achieved by using Plasticyl masterbatch. Figure 2 shows in example of surface and volume resistivity for PEEK/CNT compound. PLASTICYL™ is available in a wide range of thermoplastic resins, including PC, PP, PA, PET, HDPE, POM, ABS, PEEK and others. The knowledge for the production of PLASTICYL™ was used for the production of compounds and concentrates for veils and powdering applications.



**Figure 2.** Percolation curve for Plasticyl™ PEEK1001

### **2.2.1 Veils Application**

Thermoplastics with suitable compatibility regarding CFRC were selected. This selection was mainly based on the chemical nature of the thermoplastics. A second selection was based on the physical properties of the thermoplastics. In order to melt during the curing cycle and migrate in CFRC, melt temperature of thermoplastic should be between 110 and 135 °C. Also, the melt viscosity and MVR should be adapted to industrial veils process.

The compounds were produced using industrial twin-screw extruder and suitable information was collected to conduct the cost/risk/benefit analysis. Evaluation of those CRFC doped with CNTs veils shows an increase of through thickness electrical conductivity Kz up to 18 S.m (baseline at 4 S.m). In terms of damage tolerance, about 30 % of compression after impact and 100 % increase of G1C are observed [9].

## **2.2.1 Powdering Application**

For this application, thermoplastics with suitable compatibility regarding CFRC were selected. This selection was mainly based on the chemical nature of the thermoplastics.

The CNT-doped thermoplastic was produced on a twin-screw extruder in pellet form followed by grinding with a lab scale grinder machine. The fine powder with mean size 100µm was deposited on top of the commercial prepreg. The CFRC based doped prepreg resin showed significant increase in damage tolerance as well as compression after impact by 50 % [8, 10].

## **3. Conclusion**

Two approaches have been proposed to improve damage tolerance and electrical conductivity of CFRP. The first approach is CNT-doped thermoplastic converted in veil film and then deposited between carbon fiber laminates. The second approach is CNT-doped thermoplastic converted in fine powder and then sprinkled over prepreg plies. The results from the both technologies are interesting in term of mechanicals and electrical properties. Further investigations are ongoing to validate the concept in aeronautic and automotive applications.

# **Acknowledgments**

Nanocyl thanks AS 09 and 10 partners for their fruitful collaboration. The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under Grant Agreement No. 284562.

## **References**

- [1] Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354:56–58
- [2] J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes, and J. E. McGrath, Chemical Modification of Matrix Resin Networks with Engineering Thermoplastics: I. Synthesis, Morphology, Physical Behaviour and Toughening Mechanisms of Poly(arylene ether sulphone) Modified Eoxy Networks. *Polymer (London),* 32, 2020-2032, 1991
- [3] Hyun Sung Min and Sung Chul Kim, Fracture toughness of polysulfone/epoxy semi-IPN with morphology spectrum. *Polymer Bulletin*, 42: 221-227.
- [4] B.G. Min, J.H. Hodgkin, Z.H. Stachurski, Reaction mechanisms, microstructure, and fracture properties of thermoplastic polysulfone-modified epoxy resin. *Journal of Applied Polymer Science*, 50:1065-1073, 1993.
- [5] Bong Sup Kim, Tsuneo Chiba, Takashi Inoue, Phase separation and apparent phase dissolution during cure process of thermoset/thermoplastic blend. *Polymer*, 36: 67-71, 1995.
- [6] Metha Rutnakornpituk, Thermoplastic Toughened Epoxy Networks and Their Toughening Mechanisms in Some Systems. *Naresuan University Journal*; 13: 73-83, 2005.
- [7] Ramirez, V.A., Hogg, P.J., Sampson, W.W.: The influence of the nonwoven veil architectures on interlaminar fracture toughness of interleaved composites. *Composites Science and Technology,* 110: 103-110, 2015.
- [8] Flórez S, Gayoso J. Enhancement of primary structure robustness by improved damage tolerance, *Smart Intelligent Aircraft Structures (SARISTU) Proceeding of the Final Project Conference*, 2015.
- [9] Latko P, Boczkowska A. Fabrication of carbon nanotube doped veils, *Smart Intelligent Aircraft Structures (SARISTU) Proceeding of the Final Project Conference,* 2015.
- [10] Vavouliotis A, Sotiriades G, Kostopoulos V. Multi-scale reinforced pre-pregs for the improvement of damage tolerance and electrical properties of aeronautical structures, *Smart Intelligent Aircraft Structures (SARISTU) Proceeding of the Final Project Conference,* 2015.