# FRACTURE TOUGHNESS OF CARBON FIBER COMPOSITES BASED ON MODIFIED EPOXY CARBON NANOTUBES

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## Abstract

*Carbon nanotubes (CNT) possess excellent intrinsic characteristics like exceptionally high mechanical and conductive properties which makes them the prime candidate to reinforce high performance composite structures. However, to transfer these individual properties is still a big challenge which is often due to their bad dispersion in the matrix. The importance of CNT dispersion, their stability through-out the processing cycle, interfacial properties of CNT with different matrices are even more critical issues to finally realize the full potential of CNT. Over ten years, Nanocyl has developed a good experience to resolve these issues by following different approach such as improved innovative mixing process, CNT surface modification (functionalization) or by adding some dispersing agents or compatibilizers. Furthermore, epoxy material which is widely used as matrix for fiber reinforced composites suffers from brittleness and crack propagation. Incorporation of CNT's was proposed as a potential technique to overcome this drawback.*

*In the present work CNT's are integrated with epoxy matrix in addition to unidirectional carbon fibers (CF). After dispersing CNT's in the matrix with and without additives, unidirectional prepregs were produced subsequently composite laminates in autoclave. Mechanical tests (tensile, interlaminar shear strength-ILSS and fracture toughness) were performed. Rheological behavior of different dispersion was investigated.*

## 1. Introduction

In many applications as wind turbines, vehicles and sport goods, structural composites are subjected to fatigue loading. Delamination is one of the most predominant and life-limiting failure mechanisms in composite structures. The growth of delaminations is usually accompanied by a loss of composite stiffness which then quickly leads to final failure of the system. The interlaminar fracture toughness of fiber reinforced composites is an important property that characterizes material resistance to delamination.

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 [1-5]. Nowadays is also frequently toughening the matrix with nano-scale particles as carbon nanotube to further enhance the mechanical properties. The good mechanical properties of Carbon Nanotubes (CNTs) have made them attractive fillers in polymer matrices. CNTs can offer both interlaminar and intralaminar reinforcement, thereby providing better delamination resistance and through-thickness properties without compromising the in-plane performance. The alignment of CNTs with respect to the fiber orientation and the matrix also plays a key role in the determination of the interlaminar properties of the fiber reinforced composite.

Failure of composites reinforced with CNTs usually involves the pull-out or rupture of CNTs which consumes additional energy and thus contributes towards improved toughness [6]. An improvement in the matrix dominated properties by 8-30% has been observed using short beam shear (SBS) and compression shear tests (CST). Significant improvement has been observed in the mode-I and mode-II fracture toughness for CNT/epoxy carbon fiber reinforced composites [7].

This paper presents a work on the delamination behavior of carbon fibre/epoxy laminates. The epoxy was modified by adding carbon nanotubes and additive for toughening epoxy. Double-cantilever beam (DCB) mode I delamination tests were conducted to characterize a resistance to delamination of composites.

## 2. Materials, composites production and testing methods

### *2.1. Materials*

The raw materials used in this study are, a unidirectional Carbon fiber reinforcements manufactured by Unicarbon with an areal density of 300 g/m². The CNT modified resin is prepared from a master batch EPOCYL NC R128-06. It is based on a liquid Bisphenol-A (Bis-A) epoxy resin and contains a high concentration of NC 7000 multi-wall carbon nanotubes (MWCNTs) and additive polymer for toughening effect. MWCNTs have an average diameter of 9.5 nm, a length of several microns, and specific surface of 250–300 m²/g and a carbon purity > 90%.  The neat resin used to produce a composite without CNTs is Epoxy Epikote 828 and the hardener is Aradur 5021 from Huntsman based on dicyandiamide preparation. Ratio of hardener/epoxy is 26/100 grams. The same resin is also used to dilute the master batch with nanotubes to produce a CNT modified composite.

Prior to composite production, the effect of CNTs on the matrix viscosity is investigated. The viscosity measurements are done with an Anton Paar Rheometer at a frequency of 10 rad/s and 1% of strain. The viscosity of the neat resin as well as of masterbatch diluted 6 times with neat resin is measured as a function of temperature.

### *2.2. Composite production*

The first step in the manufacturing of the composites involves the pre-impregnation of the uni-directional carbon fibers with the resin and hardener mixture to produce prepregs. The impregnated fiber reinforcements for each resin system were then cut into prepreg plies of 20cm x 20cm and stacked on top of each other, with fourteen plies in each stack. A pre-crack (Si paper of 34 µm of thickness) was inserted in between the seventh and eighth ply of the prepreg stack. An autoclave was used to consolidate the stack to produce composite plates. The curing cycle consisted of heating at 2°C/min from room temperature to 130$^{o}$C, keeping 2 hour at 130°C and cooling to 25°C at 2°C/min. Pressure applied during consolidation was 3 bars. Three plates were produced; neat resin referred in the text as REF, resin with toughened additive referred as REF+Add and resin additive and CNTs referred as Epocyl 128-06.

### *2.3. Mechanicals testing*

Five samples from each composite plate were prepared for testing of the mode -I fracture toughness using the Double Cantilever Beam (DCB) test. The test was performed in accordance with ASTM D5528 standard. The samples thickness is around 3 mm with a width of 20mm. The pre-crack length was maintained at 56mm which meet the standard for the test. The Instron 4505 machine was used with a load cell of 5 KN. The setup was programmed for a crosshead speed of 2mm/min and the crack propagation was followed using a camera attached to the instrument. The displacement, force and crack advance at the important points were recorded. The fracture toughness values were calculated using the Modified Beam Theory. Volume fiber fraction is measured taking into count a thickness of the specimen and the number of layers

## 3. Results and discussion

Thanks to the use of modified epoxy resin based Nanocyl technology, a viscosity profile of epoxy carbon nanotube is almost the same as the neat epoxy. This means that in one hand CNTs modified epoxy could be processed as the same manner as the neat epoxy and in other hand CNT's are not agglomerated during processing.

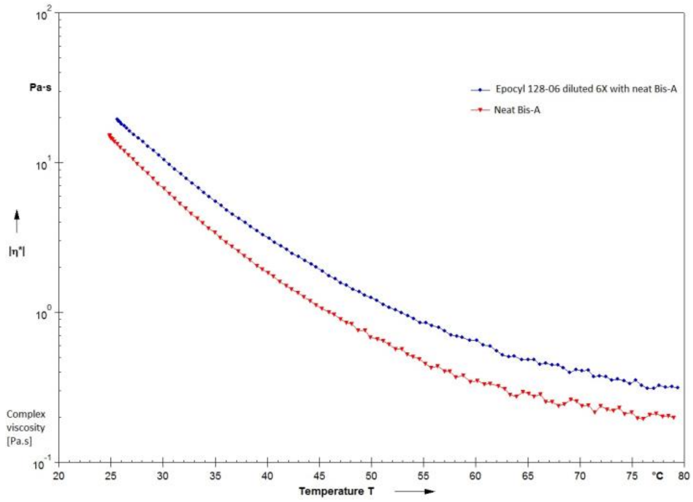


**Figure 1.** Viscosity profile for neat epoxy and modified epoxy.

The results of delamination fracture toughness of the laminates are shown in Figure 2. Compared to the composite with the neat epoxy resin, GIC of the composites are increased by the presence of the additive toughening epoxy by almost 25% and more than 90% for a combination of additive and CNTs system. The highest GIC achieved in Epocyl system is probably related to the synergetic effect between CNTs and additive. Crack deflection and crack pinning induced by the presence of CNTs in one hand and probably cavitation induced by the presence of additive in another hand are mainly the mechanisms of toughening epoxy. Scanning Electron Microscopy SEM will be done in order to assess this hypothesis.

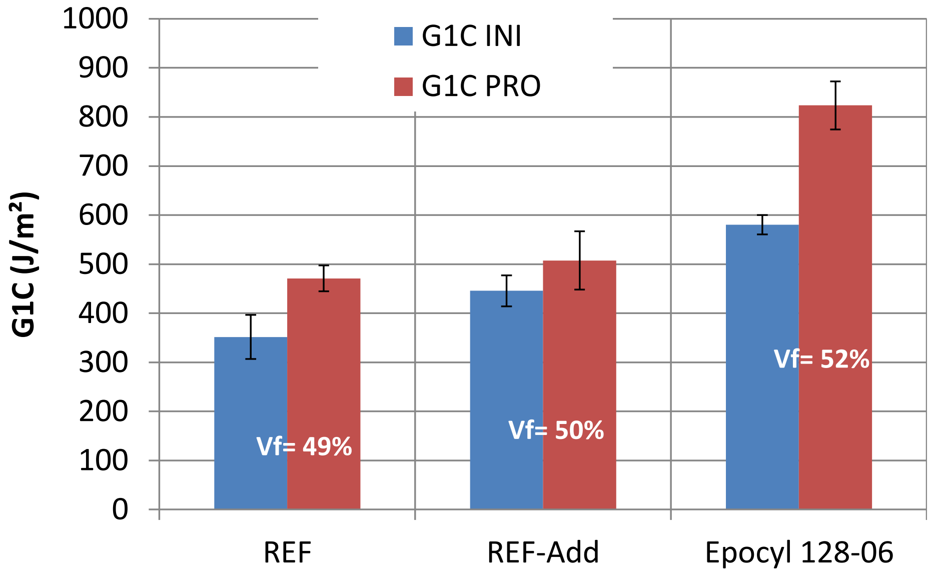


**Figure 2.** Mode I fracture toughness for neat epoxy and modified epoxy.

It is well known that the addition of additive to toughen the epoxy is always accompanied by a decrease for other thermo-mechanicals properties such as glass temperature transition and E-modulus. By adding CNTs to the formulation based epoxy modified additive toughening no decrease were measured for the other properties as can be shown in the Table 1.

| Properties | Standard | Unit | Unmodified resin | EPOCYL™ NC 128-06 |
|---|---|---|---|---|
| Transversal tensile test (perpendicular to the fiber direction) | | | | |
| Tensile Modulus | ASTM D3039 | [GPa] | 8.5 | 8 |
| Tensile Strength | ASTM D3039 | [MPa] | 80 | 90 |
| Longitudinal tensile test (fiber direction) | | | | |
| Tensile Modulus | ASTM D3039 | [GPa] | 118 | 115 |
| Tensile Strength | ASTM D3039 | [MPa] | 1400 | 1410 |
| ILSS | ASTM D2344 | [MPa] | 63 | 62 |
| Tg | DSC | °C | 128 | 128 |

**Table 1.** Thermo and mechanicals properties for neat epoxy and CNT's modified epoxy.

## Conclusion

The aim of this study is to investigate the synergetic effect of carbon nanotubes and the additive polymer into the epoxy resin. Fracture toughness of carbon laminates with carbon nanotubes and additive polymer has been studied using DCB test. The toughening effect of CNTs combined to the additive added to the epoxy is more significant than additive polymer alone.

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