

# CARBON NANOTUBE ENHANCED COMPOSITE MATERIALS

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## ABSTRACT

Non covalent functionalization by  $\pi$  stacking was accomplished by treating multi walled carbon nanotubes (MWNTs) through the use of Kentera<sup>TM</sup>, a conjugate rigid rod polymer. The functionalized MWNTs were then introduced into the epoxy resins through a combination of shear and elongation forces. The resulting epoxy resin (containing MWNTs) was then impregnated with carbon fiber under hot-melt conditions to produce epoxy pre-preg. Composites were fabricated from both epoxy resin and prepreg by hand lay ups and cured in autoclave. Mechanical testing showed about 50% and 25% improvements in flexural strength and modulus respectively. Furthermore, SEM, DMA, and mechanical test data of the composites suggested formation of strong interfacial bonding between the MWNTs, epoxy matrix and carbon fiber.

## 1. INTRODUCTION

There is a growing interest in the use multifunctional space radiation shielding materials that will provide EMI shielding and enhanced thermal conductivity, while also possessing the necessary mechanical strength to survive micro-meteor impacts. With their high-aspect ratio, small diameter, lightweight, high mechanical strength, high electrical and thermal conductivity, and unique optoelectronic properties, carbon nanotubes (CNTs) have been termed by experts as the “material of the 21<sup>st</sup> century” [1]. Due to their high polarizability and smooth surface, CNTs form strong van der Waals interactions between one another, reaching approximately 500 eV per micrometer of nanotube length [2]. The lack of processability and the difficult manipulation in host matrix have imposed great limitations to the use of CNTs in various applications. Using CNTs as a reinforcing component in polymer composites requires the ability to tailor the nature of the CNT surface to control the interfacial interactions between the CNT and the polymer chains. These interactions govern the load-transfer efficiency from the polymer to the nanotubes and the efficiency of the reinforcement. While fundamental research of CNTs focuses on the intrinsic properties of individual tubes, many commercial applications heavily rely on the interactions of bulk nanotubes with their environment. Furthermore, research shows that unfunctionalized sidewalls produce poor adhesion between the nanotubes and the polymer matrix. As a result, previous research has failed to produce nanotube/polymer composites that fully realize CNTs’ important properties [3]. In order to overcome traditional difficulties in CNT integration, and to enable preparation of CNT-reinforced composites, a large-scale effort has been invested into the development of an efficient surface treatment and functionalization technique for improving the dispersion and interfacial interaction of CNTs with various matrices. To date, the main approaches for the surface modification of CNTs can be grouped in two broad categories: 1) Covalent functionalization through reactions onto the  $\pi$  -conjugated skeleton of

CNTs, and 2) Non-covalent adsorption or wrapping of various molecules on the sidewall of CNTs.

Covalent functionalization has been widely investigated and has produced an array of modified nanotube structures bearing small molecules, polymers, and inorganic species [4]. However, sidewall functionalization of CNTs is strongly dependent on the CNT diameter. Furthermore, changes to CNT properties caused by covalently attached functional groups can be dramatic and permanent and are not always controllable. Adding any covalent functionality to the CNT inevitably changes the CNTs' electronic structure and might not be suitable for applications that rely on high electrical and thermal conductivity of CNTs. As a result, the desired multifunctionality of CNTs might be sacrificed. For example, Zhu et al [5] demonstrated that a 25% increase in the tensile strength of the epoxy was observed with the addition of 1%wt of covalently functionalized CNTs. However, this respectable mechanical enhancement was achieved at the cost of a significant loss of the CNTs electrical and thermal conductivities (due to covalent functionalization). Additionally, this approach was not amenable to scale-up for high-volume, high-rate production.

Recognizing the disadvantages associated with covalent functionalization approaches for surface modification of CNTs, Zyvex Performance Materials developed a non covalent, non-wrapping approach viz., Kentera™, a versatile and non-damaging chemistry platform that used rigid conjugated polymers, poly (aryleneethynylenes) (PAEs) [6, 7] (Figure 1). The rigid rod backbone of Kentera is designed to adhere to the surface of the CNT while the side chains are designed for enhanced compatibility, adhesion to the host matrix, and creation of a steric-barrier that prevents aggregation (i.e., clumping) of the nanotubes (Figure 1a and 1b). The major interaction between the polymer backbone and nanotube surface occurs through  $\pi$ -  $\pi$  interaction. Although  $\pi$ -  $\pi$  interaction is a weaker bond than covalent bonding, the sum of  $\pi$ -  $\pi$  interactions creates a large net-stabilizing energy that results in superior and stable systems.

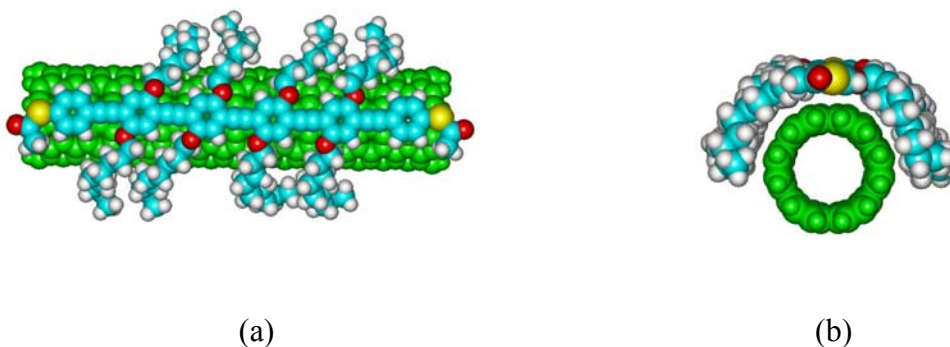


Figure 1: Lateral (a) and cross-sectional (b) representation of Kentera functionalized SWNTs.

The ease of integrating CNTs into a large array of diverse polymer matrices exemplifies the versatility of the Kentera technology. The Kentera platform technology, as depicted in Figure 2, enables us to finely tune Kentera to disperse CNTs in selected systems (S1 through S4 in figure 2). The side chains (X, Y, and Z) extending from the aryl rings of the polymer can be

manipulated to provide functional groups, such as amines, alcohols, epoxies, olefins, carbonyls and carboxylates etc that are compatible with the resins/solvents.

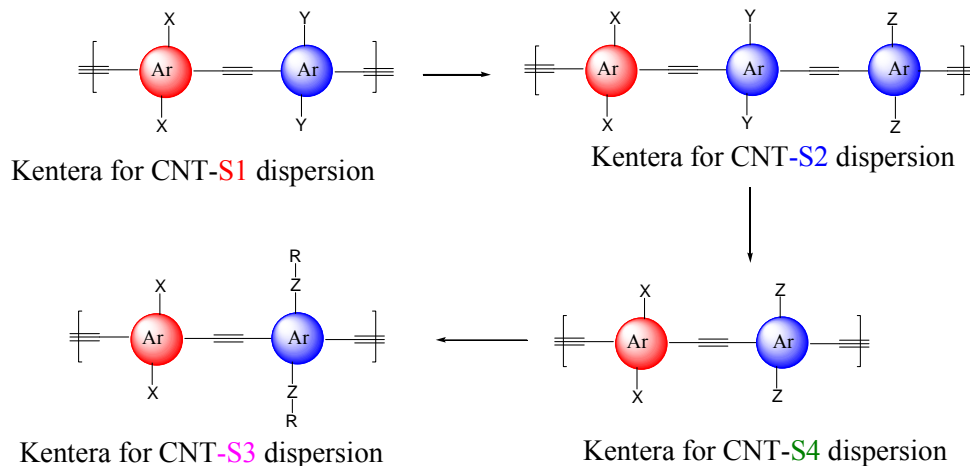


Figure 2: Representation of Kentera platform technology

Our approach dramatically reduced new product development life cycles and facilitated the incorporation of the CNTs into thermoplastic, thermoset, hydrophilic and hydrophobic matrices. Furthermore, Kentera functionalized CNTs have a form that is suitable for facile integration into the resin matrix/solvent and are readily scalable. Figure 3 shows various product lines currently amenable through the Kentera technology. For paucity of space the current paper is focused on the mechanical property enhancements achieved in epoxy (thermoset) composites.

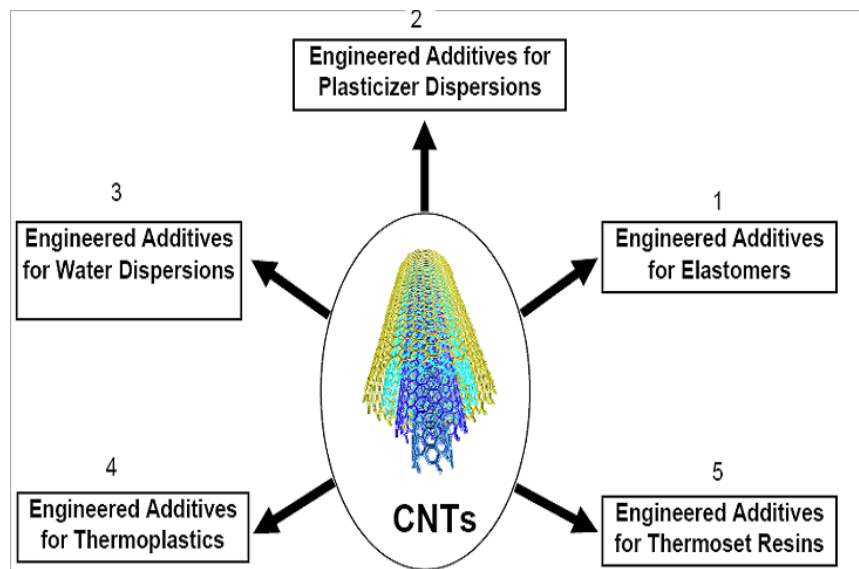


Figure 3: Easy integration of Kentera functionalized CNTs into various product lines

## **2. EXPERIMENTATION**

### **2.1 Materials and Instrumentation**

Graphstrength C100 multiwall carbon nanotubes (MWNTs) were procured from Arkema and were used without further purification along with ACS grade solvents. Epons and Epikure W were purchased from Hexion. UV/Visible spectra were obtained using absorption measurements of dispersion and were carried out in chloroform. Molecular weights of Kentera were measured against polystyrene standards in THF using Waters 150C GPC; AM GPC Gel Linear/5 micron column and Differential viscometer. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker DMX300 at 25 C using the deuterated solvent. Thermo Dynamic Analyses of resin panels and composite panels were performed by TA DMA Q-800. The data are generated by three point bending at a sinusoidal strain of 0.05% and a frequency of 1.00 Hz. Mechanical testing was carried out by Instron 5567 according to ASTM D 790. The images of Scanning Electron Microscope were taken by LEO and ZEISS.

### **2.2 General polymerization procedure for the preparation of Kentera**

Kentera was prepared by a well documented Pd-catalyzed coupling of terminal alkynes to aromatic bromides or iodides in amine solvents through Heck-Cassar-Sonogashira-Hagihara reaction conditions [8, 9, and 10]. Consistent molecular weights were obtained when monomers with greater than 90% purity were used. PAEs are rigid rods and are highly anisotropic. Molecular weight determination of rigid rods using GPC by comparing with polystyrene leads to overestimation of degree of polymerization (DP) [11]. Alternatively, DP of these polymers based on  $M_n$  can be determined by end group analysis using  $^1\text{H}$  NMR [12].

### **2.3 Functionalization of CNT**

Kentera is readily soluble in a wide variety of solvents that are commonly used in epoxy processing. The solvents include but are not limited to MEK, toluene, chloroform, acetone, NMP and THF. The concentration of Kentera in solvents is very crucial in achieving consistent functionalization. Functionalization of carbon nanotubes (CNTs) involves separation of the CNTs and binding of the Kentera polymer to the CNTs. CNTs and the Kentera polymer were mixed with a suitable solvent. The separation (exfoliation) of the CNTs was achieved by passing CNT solvent slurry through a shear mixing process for 30 – 60 minutes. The resulting functionalized CNT material was filtered to remove the solvent and dried.

### **2.4 Integration of functionalized CNTs into resins and pepreg**

The dried CNT powder, also known as powder additive (PA), was added to epoxy resin and subjected to a combination of shear and extensional flows. The mixture was passed through an appropriate mill until the particle diameter of less than 4 microns was obtained. The viscosity of the resin progressively increases with the increasing loadings in CNTs. The formulation thus obtained by incorporating MWNTs in the Bisphenol A (BPA) or Bisphenol F (BPF) resin has Epovex™ trade name. Epovex was also pre-impregnated under hot-melt conditions with carbon

fiber tows to produce a unidirectional prepreg referred to as Arovex™. A typical unidirectional carbon prepreg consists of G30-700 standard modulus (35000 ksi) PAN based fiber (1.79 g/cc) as either 12K (300 +/- 10 gsm) or 6K (145 +/- 5 gsm) in 12" rolls with a nominal resin content of 36%.

## **2.5 Fabrication of composite panels**

In typical experiments, resin matrices can usually be processed using the same cure cycle as the unmodified (neat) resin. The resin panels without reinforcement were made by a casting method. The Epovex™ (or control) formulated resins were degassed in a vacuum oven at 60 - 80 °C and transferred to a vertical mold. The mold was prepared from two metal plates pre-treated with mold release. A 3.53 mm rubber gasket was used to control the thickness of the panels. The resins were cured in a programmable oven. The resin panels thus obtained were cut into mechanical test coupons by a modified water jet tile saw with a diamond blade.

The composite panels fabricated with neat resins as control samples and Epovex™ were made by a hand lay-up process using 10 plies of 20 cm X 20 cm squares of plain wave 3K carbon fabric stacked in the warp direction. Liquid formulated resin is applied and rolled onto each ply. The lay-up is made on a mold-release treated steel tool plate, one sheet of PTFE treated peel ply is placed on top of the stack. Fiberglass or felt breather strips are placed about 10 cm around the lay-up. Single tows of glass are placed from on top of the peel ply to the breather perimeter to allow for de-bulking and a slight resin bleed. The lay-up is vacuum-bagged and placed into the autoclave. Full vacuum at ~75 KPa is applied to the lay-up and allowed to de-bulk for 15 minutes. A temperature ramp to 121 °C at 2-5 °C/minute is applied along with a pressure ramp of 14-35 KPa/minute to 550 KPa. The vacuum is released once the pressure reaches 275 KPa. The assembly is allowed to cure at 121 °C and 550 KPa for 2 hours. The second temperature ramp to 177 °C at 2-5 °C/minute is applied along with constant pressure at 550 KPa. The pressure is then slowly released and the autoclave is cooled to below 30 °C before removing the finished panels. The cure cycle for making composite panels using Epovex™ is summarized in figure 4. Note: The second ramp of the autoclave cure cycle may be performed as a free standing post-cure if adequate cure is achieved during the first temperature hold.

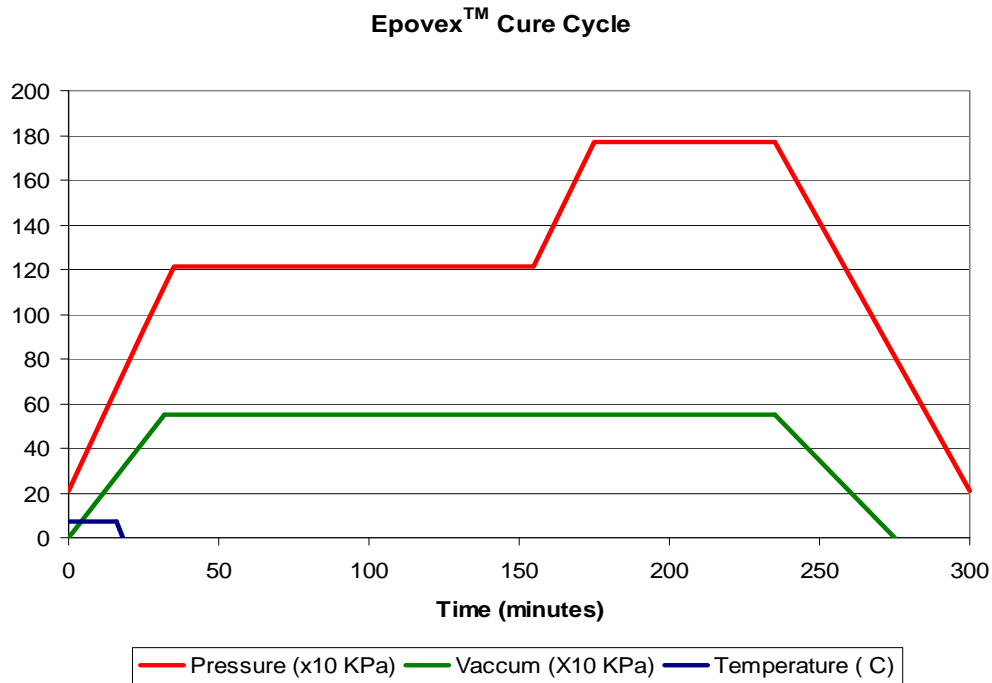


Figure 4: Cure cycle for making composite using Epovex™

Arovex™ prepreg is easily laid-up and cured using conventional methods. Eight plies of Arovex™ is cut into 30.5 cm squares and stacked in the zero degree direction. The prepreg resin content was initially 35%. The lay-up is placed on a mold release treated steel tool plate, one sheet of Teflon treated peel ply is placed on top of the stack. Fiberglass or felt breather strips are placed about 10 cm around the lay-up. Single tows of glass are placed from on top of the peel ply to the breather perimeter to allow for de-bulking and a slight resin bleed. The lay-up is vacuum-bagged and placed into the autoclave. Full vacuum at 75 KPa is applied to the lay-up and allowed to de-bulk for 15 minutes. A temperature ramp to 121 °C at 2-5 °C/minute is applied along with a pressure ramp of 14-35 KPa/minute to 550 KPa. The vacuum is released once the pressure reaches 275 KPa. The assembly is allowed to cure at 121 °C and 550 KPa for 2 hours. The pressure is then slowly released and the autoclave is cooled to below 30 °C before removing the finished panels. The cure cycle for making composite panels from Arovex™ prepreg is summarized in figure 5. The resin content of the final panel is within 1% of the original prepreg.

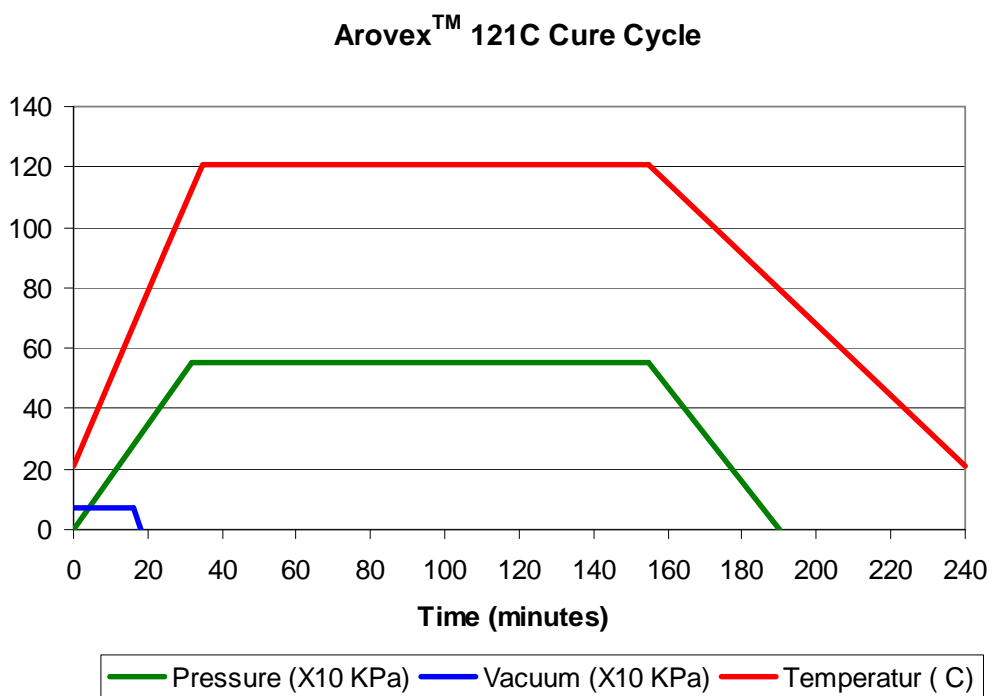


Figure 5: Cure cycle for making composite from Arovex™ prepreg

### 3. RESULTS

In order to gain fundamental understanding of the interaction of CNT with Kentera, absorption studies were performed on SWNTs (Single Walled Nanotube) because of the availability of published data for comparison. On the other hand, epoxy composites were made from MWNTs (Multi Walled Nanotube) using Kentera.

#### 3.1 Absorption studies of Kentera and SWNTs

Absorption study of functionalized SWNTs in chloroform was used to understand the interaction of CNTs and Kentera. In an effort to bring clarity to the next few sections; excerpts from an earlier published work (from our organization) are provided here. The UV-visible absorption spectra of Kentera solution, Kentera film, SWNT suspension and Kentera-SWNT solution is presented in figure 6. The lowest energy absorption band (corresponding to  $\pi$ - $\pi^*$  transition band of Kentera (green) in solution is at 440 nm, which is red-shifted to 487 nm in solid state (black). The observed 47 nm red-shift of  $\pi$ - $\pi^*$  transition band is due to the planarization of Kentera backbone in solid state, leading to better  $\pi$ -conjugation with a lower band gap. Similarly the lowest energy absorption band of Kentera-SWNT (blue) solution in chloroform is red-shifted by 65 nm to 505 nm relative to pure Kentera (green) solution. The observed 65 nm red-shift of  $\pi$ - $\pi^*$  transition band is not due to the charge-transfer interaction between Kentera and SWNT, because the charge-transfer interaction is found to be insignificant on the basis of both solid state absorption and Raman spectroscopic analysis. We can also exclude the formation of Kentera aggregate, because chloroform has good solvation characteristics. Therefore the 65 nm red-shift most likely stems from the planarization of individual Kentera backbone on the carbon nanotube

surface via  $\pi$ - $\pi$ -stacking in solution, which is also consistent with our previous study suggesting that the PAE backbone does not wrap around the SWNT. The near disappearance of free Kentera band (440 nm) in SWNT solution, as well as the solution-phase NMR spectra [6], provides strong evidence for the formation of stable and irreversibly bound complexes between Kentera and SWNT rather than a simple mixture.

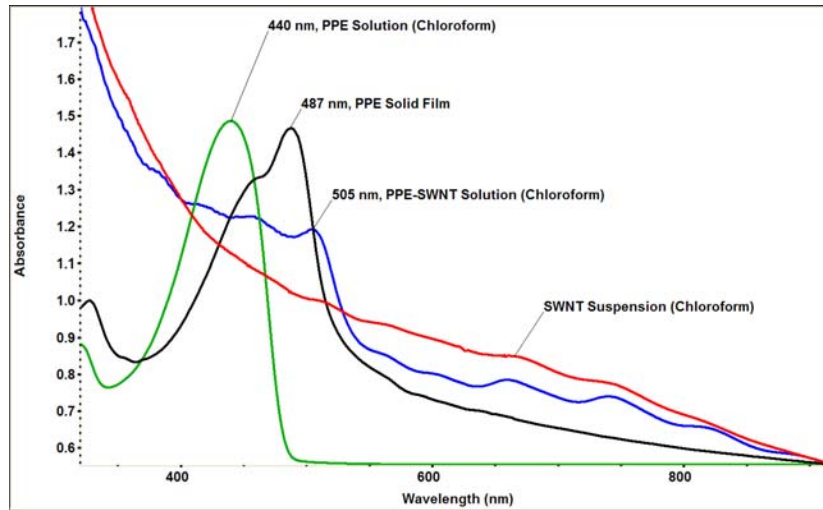


Figure 6: Absorption spectra of pure Kentera (green) solution in chloroform, pure PPE (black) solid film, SWNT suspension in chloroform (red), and Kentera-SWNT solution (blue) in chloroform.

### 3.2 The Mechanical Properties of Resin Panels and Composites Panels

Results shown in figure 7 from resin panels were used in establishing the best MWNTs loadings and optimize the process parameters for making composite panels. Resin panels were made with progressive increasing MWNT loadings to a maximum of 2% by weight. The viscosity of the resin reached 20000 cps at 1% loadings and was difficult to make resin panels at high MWNT loadings.



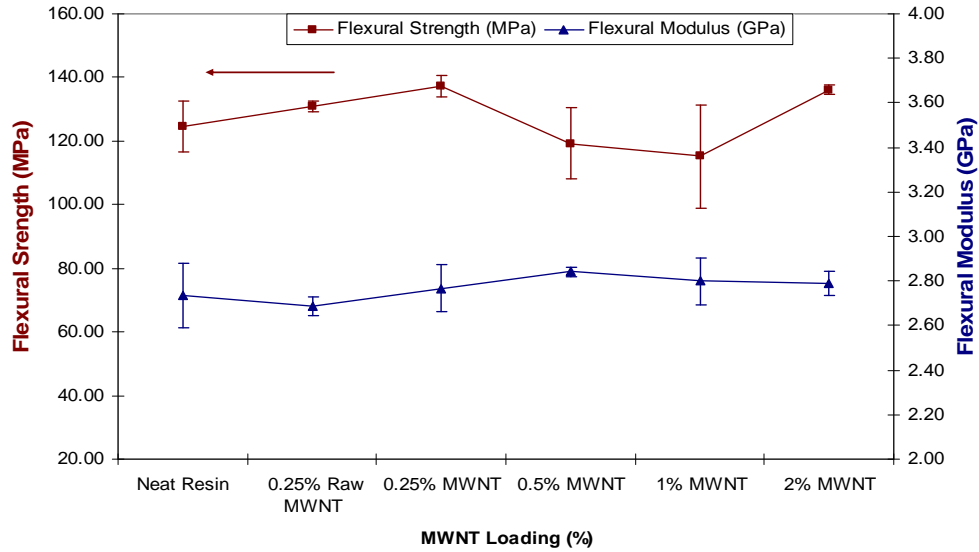


Figure 7: Comparison of mechanical properties in resin panels

The mechanical properties achieved from composite panels made from Epovex and Arovex is presented in Table 1. Improvements in flexural strength and modulus to the tune of 50% and 25% respectively were realized using Kentera technology. The observed improvements may be attributed to the excellent dispersion of MWNT in resin phase and the better interphase or interfacial bonding between resin and carbon fibers.

Table 1 – Mechanical Test Data of Enovex and Arovex

Panels	Flexural strength (MPa)	Standard Deviation	Flexural Modulus (GPa)	Standard Deviation
<b>Epovex</b>	877.8	68.2	62.9	1.2
Control	590.2	56.1	52.5	1.7
Improvement (%)	45.1		19.8	
<b>Arovex</b>	1159.4	74.2	54.0	1.6
Control	766.1	79.2	42.7	3.1
Improvement (%)	51.3		26.4	

### 3.4 Dynamic Mechanical Analysis (DMA)

Improvement in storage modulus of Epovex composite panels when compared to the neat resin panel, measured by DMA, is shown in Figure 8. An improvement of 24% observed by DMA has a strong correlation to the data obtained from Instron testing. Furthermore, strong interphase or interfacial interactions between MWNTs, resin, and carbon fibers were demonstrated from the plot of  $\tan \delta$  vs. temperature shown in figure 9. Lower  $\tan \delta$  value of the Epovex composite panel

when compared to the neat resin panel is attributed to the strong reinforcement of MWNT in the composites [14, 15, 16, and 17].

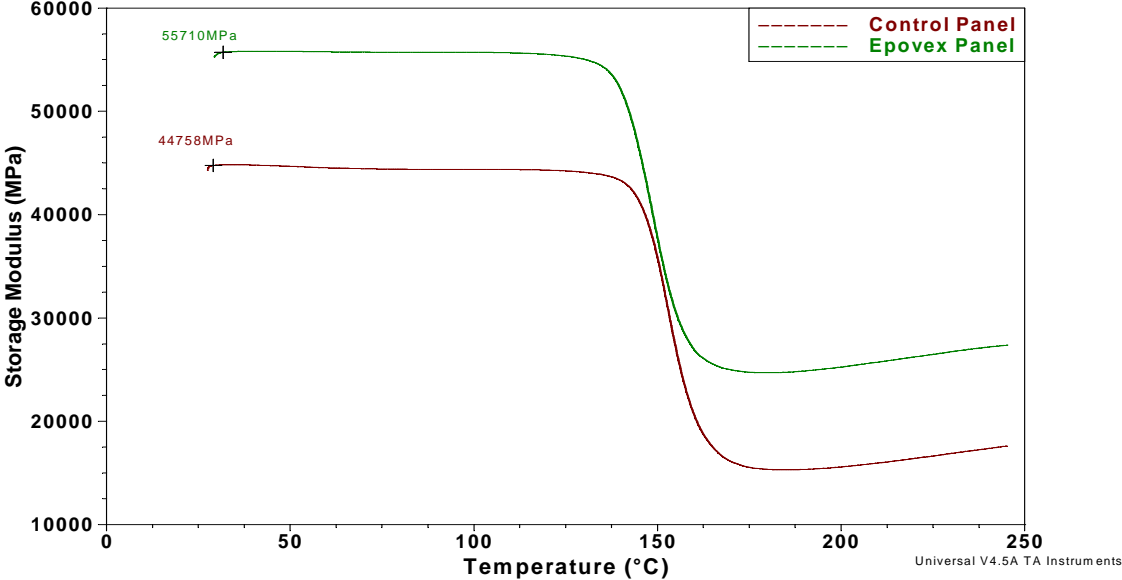


Figure 8 – Storage Modulus of Neat and Epovex Composite Panels

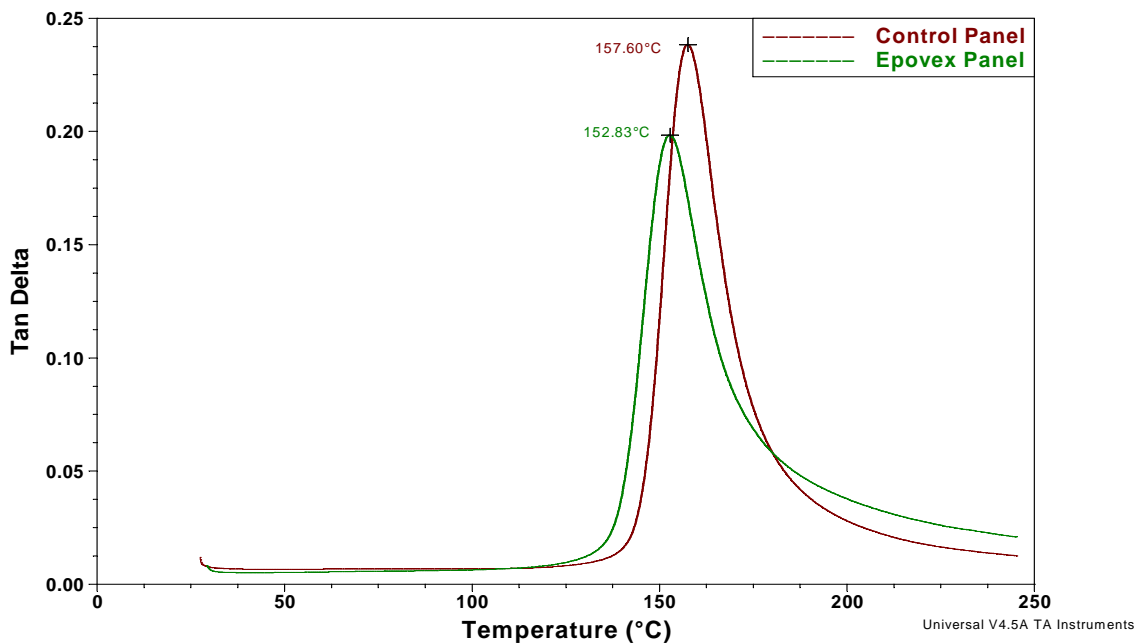


Figure 9 – Tan  $\delta$  of Neat and Epovex Panel

### 3.5 Scanning Electron Microscope analysis

SEM images of the cryogenically cracked MWNT epoxy panels (without reinforcement) provide a clear evidence for crack bridging. SEMs shown in below Figure 10, combined with mechanical data provide evidence for strong interfacial bonding between the nanotubes and the epoxy matrix. The SEM image on the right is the enlargement of the matrix crack on the left.

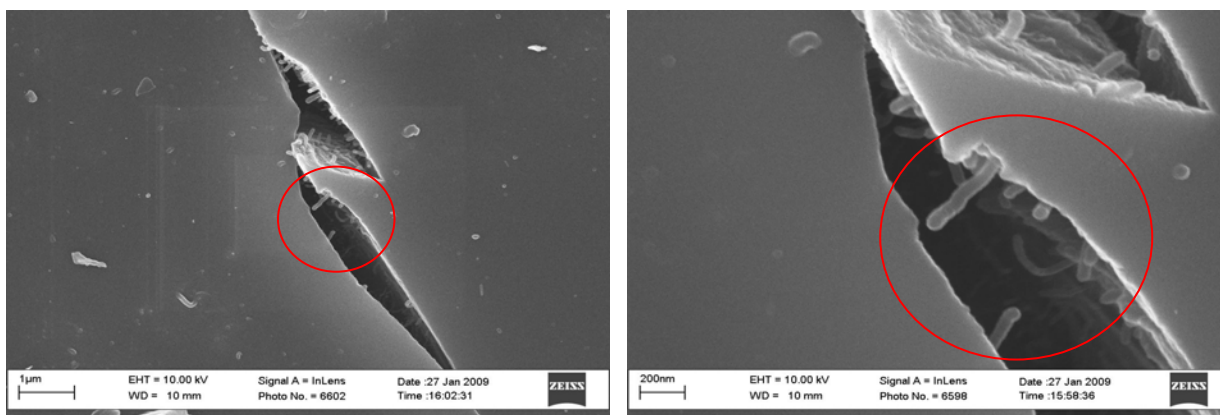


Figure 10: SEM images of the cryogenically cracked epoxy CNT composites showing the bridging of the crack by multiple MWNTs

## 4. CONCLUSIONS

An efficient and highly scalable methodology for harnessing superior properties of MWNTs in nano-composites was demonstrated through the use of Kentera, a conjugate rigid rod polymer. Intrinsic properties of MWNTs were conserved because the interaction between Kentera and MWNTs is by non covalent bonding referred as  $\pi$  stacking. For efficient  $\pi$  stacking Kentera with specific molecular weight was developed and produced using reliable synthetic methods. Kentera functionalized MWNTs were dispersed in the Bisphenol A (BPA) and Bisphenol F (BPF) matrix by a combination of shear and elongation forces. The resulting epoxy formulation was referred to as Epovex. On the other hand, carbon fiber impregnated Epovex under hot-melt conditions produced epoxy prepreg called Arovex. Our experiments seem to indicate that in order to achieve mechanical property improvements it is important to optimize MWNT loadings for specific resin system. Composites made from both epoxy resin and prepreg showed 50% and 25% improvements in flexural strength and modulus respectively. The observed improvements may be attributed to the excellent dispersion of MWNT in resin phase and the better interphase or interfacial bonding between resin and carbon fibers. Improvement in storage modulus of Epovex composite panels when compared to the neat resin panel, measured by DMA, shows an improvement of 24% and has a strong correlation to the data obtained from Instron testing. Work is currently underway to understand the relative orientation of Kentera with the surface of the MWNTs, develop a bulk method for quantifying the weight of Kentera attached to the MWNTs, and develop improved methods for functionalizing the MWNTs.

## 5. REFERENCES

1. (a) Iijima, Sumio. "Helical microtubules of graphitic carbon." *Nature* 1991, 354, 56-58. (b) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. "Physical Properties of Carbon Nanotubes", Imperial College Press, London, 1998.
2. Girifalco, L. A.; Hodak, M. Lee, R. S. "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential". *Physical Review B*, 2000, 62, 13104-13110.
3. (a) Ajayan, P. M. P.; Linda, S. S.; Cindy, G.; Angel R. "Mechanical response of single walled carbon nanotubes in polymer nanocomposites" *Adv. Mater.* 2000, 12, 750-753. (b) Breuer, O.; Sundararaju, U. "Big returns from small fibers: A review of polymer/carbon nanotube composites" *Polymer Composites*. 2004, 25, 630-645.
4. (a) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. "Chemistry of carbon nanotubes." *Chem. Rev.* 2006, 106, 1105-1136. (b) Hirsch, A. "Functionalization of Single-Walled Carbon Nanotubes." *Angew. Chem. Int. Ed.* 2002, 41, 1853-1859.
5. Zhu, J; Peng, H.; Rodriguez-Macias, F.; Margrave, J. L.; Khabashesku, N.; Imam, A. M.; Lozano, K., Barrera, E. V. "Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes." *Adv. Funct. Mater.* 2004, 14, 643-648.
6. Chen, J.; Liu, H.; Weimer, W. A.; Halls, M. D.; Waldeck, D. H.; Walker, G. C. "Noncovalent Engineering of Carbon Nanotube Surfaces by Rigid, Functional Conjugated Polymers." *J. Am. Chem. Soc.* 2002, 124, 9034-9035.
7. (a) Ait-Haddou, H.; Rutkofsky M. U.S. Patent 7,296,576. (b) Ait-Haddou, H.; Rutkofsky, M. USA patent publication 20060054866.

8. Dieck, H. A.; Heck, R. F. "Palladium catalyzed synthesis of aryl, heterocyclic and vinylic acetylene derivatives" *J. Organomet. Chem.* 1975, 93, 259-263.
9. Cassar, I. "Synthesis of aryl- and vinyl-substituted acetylene derivatives by the use of nickel and palladium complexes" *J. Organomet. Chem.* 1975, 93, 253-257.
10. Martin, R. E.; Diederich, F. "Linear Monodisperse  $\pi$ -Conjugated Oligomers: Model Compounds for Polymers and More" *Angew. Chem. Int. Ed.* 1999, 38, 1350-1377.
11. Francke, V.; Mangel, T.; Müllen, K. "Synthesis of  $\alpha,\omega$ -Difunctionalized Oligo- and Poly(p-phenyleneethynylene)s" *Macromolecules* 1998, 31, 2447-2453.
12. (a) Kloppenburg, L.; Jones, D.; Claridge, J. B.; zur Loye, H.-C.; Bunz, U. H. F. "Poly(p-phenyleneethynylene)s Are Thermotropic Liquid Crystalline" *Macromolecules* 1999, 32, 4460-4463. (b) Watanabe, Y.; Mihara, T.; Koide, N. "Synthesis and physical properties of novel side-chain type liquid crystalline poly(aryleneethynylene)s" *Macromol. Chem. Phys.* 1998, 199, 977-983.
13. Chen, J.; Ramasubramaniam, R.; Liu, H. *Mater. Res. Soc. Symp. Proc.* 858E, 2005, HH12.4.1-HH12.4.6
14. Fisher, F. T., Andrews, R., Brinson, L. C., Schadler, L. S., *Composites Science and technology*, 66 1159 (2006)
15. Ciprari, D., Jacob, K., Tannenbaum, R. *Macromolecules*, 2006, 39 (19), 6565
16. Carlier, V., Sclavons, M., Jonas, A. M., Jérôme, R., Legras, R. *Macromolecules*, 2001, 34 (11), 3725.
17. J. Brown, I. R., Pethrick, R. A., *Polymer International*, 2004, 53, 2130–2137.