# ELECTRIC FIELD ENABLED MANIPULATION OF CNT ALIGNMENT IN EPOXY MATRIX: METHODOLOGY AND MECHANICAL CHARACTERIZATION

Jayaram R. Pothnis[1], Dinesh Kalyanasundaram[2] and Suhasini Gururaja[3]

[1]Department of Aerospace Engineering, Indian Institute of Science, C.V. Raman Road, Bengaluru 560012, India
Email: jayaramp@iisc.ac.in
[2]Centre for Biomedical Engineering, Indian Institute of Technology Delhi, Hauz Khaz, New Delhi 110016, India
Email: dineshk@cbme.iitd.ac.in, Web Page: http://web.iitd.ac.in/~dineshk/
[3]Department of Aerospace Engineering, Indian Institute of Science, C.V. Raman Road, Bengaluru, 560012, India
Email: suhasini@iisc.ac.in, Web Page: http://www.aero.iisc.ernet.in/people/suhasini-gururaja/

**Keywords:** Carbon nanotube, epoxy, electric field, mechanical properties

## Abstract

The alignment of carbon nanotubes (CNTs) in polymer matrix is an effective way to utilize their anisotropic properties. In this study, a CNT alignment methodology based on the use of a non-uniform electric field is presented. The manipulation of CNT behaviour in an epoxy matrix was accomplished based on the principle of dielectrophoresis. The effectiveness of the technique was assessed by determining the tensile strength and fracture toughness ($K_{IC}$) of aligned CNT/epoxy composites samples prepared using this method. Tensile tests revealed an increase in tensile strength of nanocomposites with increasing CNT loading content up to 0.1 wt.% CNT. A ~ 27 % increase in tensile strength in CNT nanocomposite samples containing 0.1 wt.% CNTs with respect to that of neat resin was observed. The fracture toughness values were also observed to increase with increasing CNT loading content. A ~ 50 % increase in $K_{IC}$ value in nanocomposites containing 0.5 wt.% CNTs was observed as compared to that of neat resin. The results indicate that the method can be effectively used to preferentially align CNTs in a polymer matrix.

## 1. Introduction

The past decade has seen remarkable efforts towards improving functionality of epoxy resins through the addition of a variety of nanofillers [1]. Mechanical, electrical, optical and thermal are some of the properties targeted for improvement in epoxies through the addition of nanoscale fillers.to the matrix [1, 2]. Nanocomposites are being integrated with conventional composites to produce multi-functional hierarchical structures to perform additional functions such as heat shielding and sensing along with structural load sharing [3]. Among nanofillers, the 1-D carbon nanotubes (CNTs) exhibiting very high anisotropic physical and mechanical properties have been widely used to impart desired functionality to epoxy matrices [4, 5]. For better utilization of CNT anisotropy, they have been alignment in polymer matrices using different methods [6]. While techniques such as mechanical stretching [7], magnetic field [8, 9], and electric field [4, 10, 11] approaches have been employed to align CNTs, electric field method has been widely used with either AC or DC fields employed to drive CNT alignment [6].

In previous studies involving electric fields, a parallel plate electrode configuration has been typically employed to generate uniform field to align CNTs in the polymer matrix. However, this approach requires the use of very high levels of voltage application to prepare samples of small dimensions. Therefore, considering scalability aspect, the approach would be difficult to pursue. Furthermore, if an application requires CNT alignment in locally in a structure and in specific directions, then the method cannot be used in the current form. The method presented in this study attempts to overcome the aforementioned limitations The present approach attempts to overcome these limitations by using a non-uniform electric field to control CNT behavior in an epoxy matrix. The method is based on the phenomenon of dielectrophoresis (DEP) [12]. In the present work, the basic methodology of CNT alignment based on dielectrophoresis is discussed initially. The effectiveness of the technique was assessed through conduct of tensile and fracture toughness tests on the samples prepared using this method. The results of the mechanical characterization tests are presented.

## 2. Experimental Studies

### 2.1. Materials

Amine functionliazed multi-walled CNTs (United Nanotech Innovations Pvt. Ltd., India) were used in the study. The dimensions of CNTs ranged from 5 nm – 20 nm in diameter and between 1 µm to 10 µm in length. Epoxy resin LY 5052 (Huntsman, Switzerland) with triethylene tetramine (TETA) (Loba Chemie Pvt. Ltd.) as curing agent was used as the matrix. The ratio of resin to curing agent was 100:13 by weight.

### 2.2. Fabrication of Nanocomposites

The CNT/epoxy mixtures containing varying contents of CNTs were prepared using a solvent removal process for effective filler dispersion [11]. Pre-heated CNTs were sonicated in acetone using a bath sonicator (40 kHz frequency) for two hours to breakdown the CNT aggregates. Measured quantity of epoxy was then added to the mixture followed by sonication for two hours further. The acetone was removed under vacuum to yield CNT/epoxy mixture containing well-dispersed CNTs. Mixtures containing 0.01 %, 0.05 %, 0.1 % and 0.5 % by weight of CNTs were prepared using the procedure. Fig. 1 presents the experimental set-up used for fabricating aligned nanocomposites. The electrode set-up consisted of a sharp tipped slender steel electrode (0.8 mm diameter) on one side (referred to as electrode A) and an aluminum strip of dimensions 20 mm x 10 mm x 1 mm on the other side (referred to as electrode B). The electrodes were placed in an area of dimensions 10 mm x 11 mm surrounded by Teflon walls of 5 mm height. The entire arrangement was mounted on a glass petridish to facilitate sample heating. A hot plate was used to supply heat. Voltage was supplied by an AC supply unit (0 - 270 $V_{rms}$ at constant frequency of 50 Hz) to the electrode set.

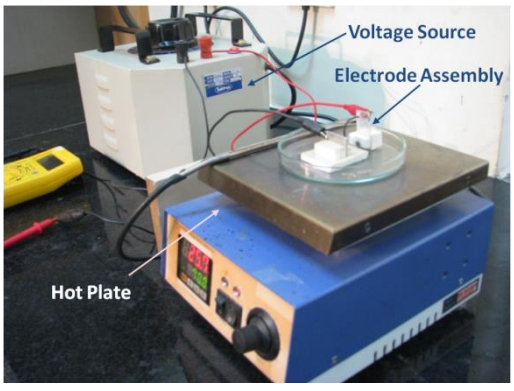


**Figure 1.** Experimental set-up to fabricate aligned CNT nanocomposites.

For sample fabrication, the degassed CNT/epoxy mixture was gently mixed with the curing agent and then transferred to the region between the electrodes. Voltage was then applied to the electrodes for 15 minutes and under the application of voltage, the sample was heated to 70 °C to preserve the alignment configuration. Fig.2 depicts a typical sample before and after the application of voltage. The solidified samples were released and post cured for two hours at 100 °C in a hot air oven. These samples were fabricated to study the CNT alignment behavior. For preparing samples for tensile testing and fracture toughness measurement, multi-electrode configurations were used to align CNTs between the electrodes. For this, four sharp tipped slender steel electrodes (0.8 mm diameter) were used on one side. These electrodes were spaced 10 mm apart. A flat aluminum strip of dimensions 50 mm x 25 mm x 1 mm was used on the other side. The samples were prepared following the same method as outlined earlier. However, considering the larger electrode gap (between sharp tipped and flat electrodes), larger voltages (350 $V_{rms}$ to 500 $V_{rms}$) were used. electrode gaps of 25 mm and 60 mm were maintained to fabricate specimens for fracture toughness measurement and tensile testing respectively. Randomly oriented CNT nanocomposite samples containing similar amount of CNTs were also prepared for comparison of properties.

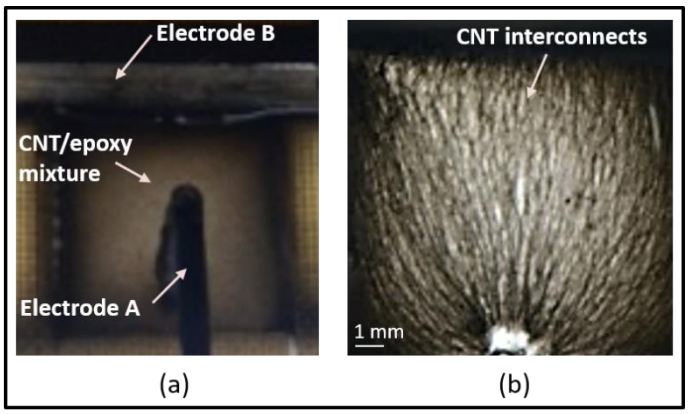


**Figure 2.** Typical aligned CNT/epoxy sample (0.1 wt. % CNT; 270 $V_{rms}$ @ 50 Hz), (a) before voltage application, (b) after voltage application

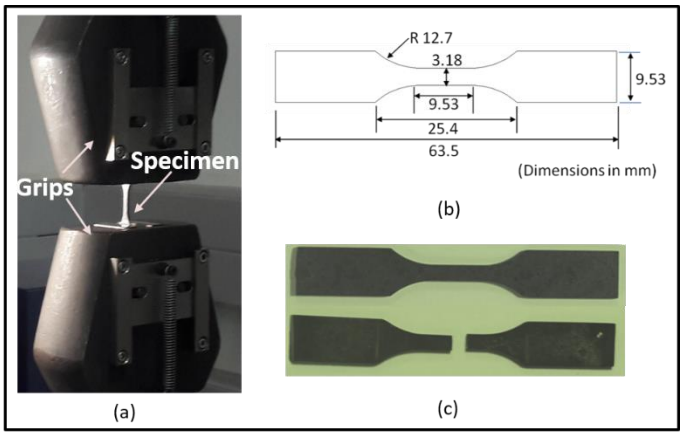


**Figure 3.** (a) Tensile test set-up, (b) Schematic of tensile test specimen, (c) Typical test specimens: before and after failure

### 2.3. Tensile and Single Edge Notch Bending (SENB) Tests

The specimens for tensile testing and SENB tests were prepared and tested in accordance to ASTM standards D638-14 and D5045-14 respectively. All the samples including neat resin samples were tested using a Mechmesin® Multitest 10-i universal testing machine. The specimens were tested at a displacement rate of 1 mm/min during both tensile and SENB tests. To avoid specimen slippage during testing, self centering grips attached to a 10 kN load cell were used during tensile tests. Fig. 3a presents photographs of a typical microtensile specimen during testing. Fig. 3b and Fig. 3c present details of the specimen dimensions and typical specimens that were tested. Sample thickness of 2 mm was used.

For the SENB tests on the same equipment, a 1 kN load cell was used. A loading bracket with a cylindrical pin at the end (3 mm diameter) was used to apply the load. Sample dimensions for SENB tests were determined based on sample thickness of 2.5 mm to 3 mm. To measure displacement, a laser extensometer was used. Fig. 4a presents the experimental set-up used to conduct the SENB tests. Fig. 4b and Fig. 4c presents the schematic of the loading arrangement and typical specimens that were tested to determine the fracture toughness. The specimens were cut to dimensions using waterjet.

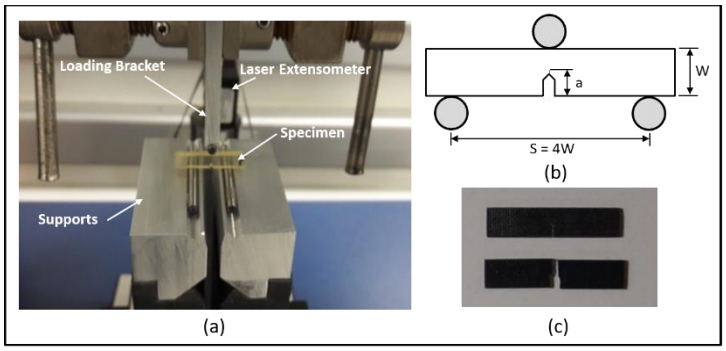


**Figure 4.** (a) Set-up for SENB tests, (b) Schematic of specimen loading, (c) Typical specimens: before and after testing

## 3. Results and Discussion

### 3.1. CNT Alignment in Epoxy Matrix

In the present study, a non-uniform electric field was generated between the electrodes to manipulate CNT behaviour. Fig. 3b shows the alignment of CNTs within the epoxy matrix in case of a 0.1 wt.% CNT nanocomposite sample when the applied voltage was 270 $V_{rms}$. In the presence of an electric field, CNTs experience electrokinetic forces such as electroosmotic force, DEP force and electrothermal forces [12]. However, considering the frequency of applied voltage (50 Hz), DEP force would be the dominant force [13-15] acting on the individual CNTs. In addition to DEP force, the CNTs also experience DEP induced torque. The DEP induced force ($F_{DEP}$) and torque ($T_{DEP}$) experienced by CNTs is given by [12, 16]:

$$F_{\mathrm{DEP}} = \frac{\pi r^2 l}{3} \varepsilon_{\mathrm{m}}\, Re\, [CM]\, \nabla(E_l^2) \tag{1}$$

$$T_{DEP} = \frac{\pi r^2 l}{2} \varepsilon_m Re \left[ \frac{(\varepsilon_p^* - \varepsilon_m^*)^2}{[\varepsilon_m^* + (\varepsilon_p^* - \varepsilon_m^*) L_l]\,(\varepsilon_p^* + \varepsilon_m^*)} \right] E^2 sin2\theta \tag{2}$$

Here, $r$ and $l$ refer to CNT radius and length. $\varepsilon^*$ refers to complex permittivity and $\varepsilon$ refers to permittivity with the subscripts $m$ and $p$ indicating corresponding values for medium and particle. $\theta$ is the orientation

angle of CNT with respect to the electric field, $E$ is the applied electric field, $E_l$ is the component of electric field in length direction of CNT and $CM$ is referred to as the Clausius-Mossotti factor. $L_l$ is referred to as the depolarization factor along the longitudinal axis of the particle [16]. The value of CM factor (positive or negative) determines the direction of CNT movement and is evaluated using Eqn. 3 [12]. For the present case, $CM$ value evaluated to be positive indicating CNT movement towards the electrode with higher potential.

$$CM = \left[\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_m^* + (\varepsilon_p^* - \varepsilon_m^*)L_l}\right] \quad (3)$$

During the experiments, the alignment of CNTs was observed to initiate near the electrode of higher potential (electrode A) where the electric field strength was the highest. With increasing time of voltage application, macroscopic alignment of CNTs was observed to increase with the formation of interconnects eventually leading to the formation of CNT network as seen in Fig. 3b.

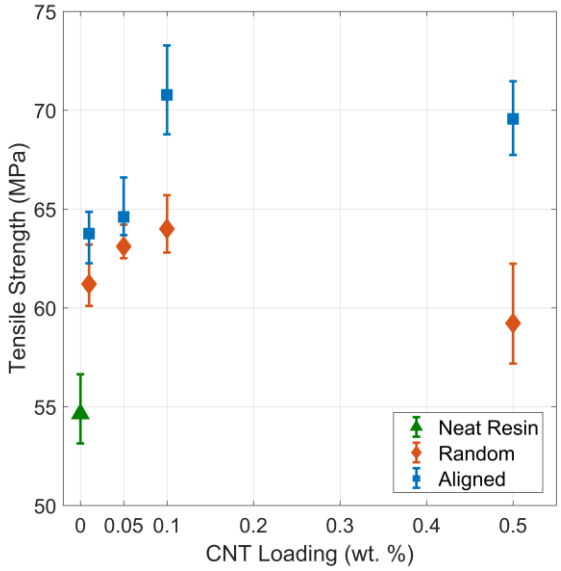


**Figure 5.** Tensile strength of randomly oriented and aligned CNT nanocomposites as a function of CNT content.

### 3.2. Tensile Strength of Nanocomposites

The variation of tensile strength with increasing CNT loading can be seen in Fig. 5. In the figure, random refers to randomly oriented CNT nanocomposite samples. With increasing CNT content, the tensile strength was observed to increase up to 0.1 wt. % CNT loading in case of both aligned and randomly oriented CNT samples. In case of randomly oriented samples, a decrease in strength was observed for 0.5 wt.% samples. However, in case of aligned samples with the same CNT loading, the tensile strength value remained nearly the same as seen in 0.1 wt.% samples. The increase in strength in nanocomposite samples can be attributed to better interfacial interaction of amine functionalized CNTs with the epoxy matrix [4, 5]. Amine functionalized CNTs have hhigher surface energy and higher wettability compared to epoxy leading to improved properties [1]. The results are similar to those reported earlier [17]. The decrease in tensile strength in case of 0.5 wt.% CNT samples is attributed to the CNT agglomerates that may be present in samples as CNT loading content increases.

At a CNT loading of 0.1 wt. %, 27 % improvement in tensile strength was seen as compared to that of neat resin. Compared to tensile strength of samples containing randomly oriented CNTs, a maximum increase of approximately 10 % was observed for the 0.1 wt. % CNT samples. For composites with lower CNT content (0.01 wt. % and 0.05 wt. %), marginal improvements in tensile strength was observed. This can possibly be due to greater spacing between individual CNTs reducing alignment effectiveness. With increasing CNT loading, the average distance between the individual CNTs is lower. In the presence of a non-uniform electric field, this facilitates greater alignment of CNTs.

### 3.2. Fracture Toughness of Nanocomposites

SENB tests were conducted to determine $K_{IC}$ values of neat resin, randomly oriented CNT and aligned CNT samples. In case of aligned nanocomposites, the samples were cut in a manner that the crack propagation direction was perpendicular to the CNT alignment direction. Table 1 presents the variation of $K_{IC}$ values with increasing CNT loading and normalized with respect to neat epoxy $K_{IC}$ value. The values are presented as ratio $K_{IC,c}$ / $K_{IC,\ m}$, where suffixes *c* and *m* refer to composite and matrix respectively. In the table, random refers to randomly oriented CNT nanocomposite samples. In case of both aligned and random CNT samples, with increasing CNT content, the fracture toughness was observed to increase indicating the benefit of CNT addition to epoxy matrix. However, the increase was higher in case of the aligned CNT samples. Nearly 50 % increase in fracture toughness value was observed in case of aligned 0.5 wt.% CNT samples. The increase in fracture toughness is attributed to crack pinning, crack bridging and crack deflection mechanisms [9, 11]. It can also be observed that the incremental increase in fracture toughness reduces with increasing CNT content. This is due to reduced effectiveness of CNT alignment at higher CNT loading due to higher mix viscosities restricting CNT alignment.

**Table 1.** Normalized fracture toughness with varying CNT loading content

| Specimen Type | $K_{IC,\ c}$ / $K_{IC,\ m}$ | | | |
|---|---|---|---|---|
| | Random | | Aligned | |
| | Normalized Value | Std. Dev. | Normalized Value | Std. Dev. |
| Neat Resin | 1 | | | |
| 0.01 wt. % CNT | 1.11 ± 0.02 | 0.02 | 1.17 ± 0.04 | 0.03 |
| 0.05 wt. % CNT | 1.20 ± 0.09 | 0.03 | 1.36 ± 0.16 | 0.19 |
| 0.10 wt. % CNT | 1.18 ± 0.21 | 0.21 | 1.44 ± 0.02 | 0.02 |
| 0.50 wt. % CNT | 1.26 ± 0.08 | 0.10 | 1.50 ± 0.11 | 0.08 |

## 4. Conclusions

In this work, a novel method to align CNTs in epoxy matrix was presented. The alignment of CNTs was achieved using a non-uniform electric field. The effectiveness of the alignment method was evaluated through mechanical characterization tests. Significant increase in tensile strength was obtained due to CNT alignment in the matrix. However, with increasing CNT content, a decrease in CNT alignment effectiveness was observed. The fracture toughness values also increased significantly due to CNT addition in epoxy matrix. The fracture toughness values of aligned CNT samples with CNT alignment perpendicular to crack propagation direction were much higher as compared to that of the randomly oriented CNT samples. The effectiveness of the alignment method was demonstrated.

**Acknowledgments**

The authors are thankful to Naval Research Board, Defence Research Development Organization (DRDO), India for funding this work. The mechanical characterization tests were carried out at Micro and Nano Characterization facility (MNCF) located at CeNSE, IISc, Bangalore funded by NPMAS-DRDO and MCIT, Government of India.

**References**

[1] S. Liu, V.S. Chevali, Z. Xu, D. Hui, and H. Wang. A review of extending performance of epoxy resins using carbon nanomaterials. *Composites Part B: Engineering*, 136:197–214, 2018.

[2] V. D. Punetha, S. Rana, H. J. Yoo, A. Chaurasia, J. T. McLeskey, M. S. Ramasamy, Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene, *Progress in Polymer Science*, 67: 1–47, 2017.

[3] G. Mittal, K.Y. Rhee, V. Mišković-Stanković, and D. Hui. Reinforcements in multi-scale polymer composites: Processing, properties, and applications. *Composites Part B: Engineering*, 138: 122–139, 2018.

[4] P. Gupta, M. Rajput, N. Singla, V. Kumar, D. Lahiri, Electric field and current assisted alignment of CNT inside polymer matrix and its effects on electrical and mechanical properties, *Polymer*, 89: 119-127, 2016.

[5] N. Domun, H. Hadavinia, T. Zhang, T. Sainsbury, G.H. Liaghat, and S. Vahid. Improving the fracture toughness and the strength of epoxy using nanomaterials – a review of the current status. Nanoscale, 7(23): 10294–10329, 2015.

[6] P. S. Goh, A. F. Ismail, B. C. Ng, Directional alignment of carbon nanotubes in polymer matrices: Contemporary approaches and future advances, *Composites Part A: Applied Science and Manufacturing*, 56 : 103-126, 2014.

[7] X.W. Zhao, and L. Ye. Structure and properties of highly oriented polyoxymethylene/multi-walled carbon nanotube composites produced by hot stretching. *Composites Science and Technology*, 71: 1367–1372, 2011.

[8] J. Haibat, S. Ceneviva, M.P. Spencer, F. Kwok, F., S. Trivedi, S.E. Mohney, and Yamamoto, N. Preliminary demonstration of energy-efficient fabrication of aligned CNT-polymer nanocomposites using magnetic fields. Composites Science and Technology, 152: 27–35, 2017.

[9] Ma C, Liu H-Y, Du X, et al. Fracture resistance, thermal and electrical properties of epoxy composites containing aligned carbon nanotubes by low magnetic field. *Composites Science and Technol*ogy, 114: 126–135, 2015.

[10] M.W. Wang, N.I. Yu, and W.H. Liao. Aligned MWCNT-reinforced bulk epoxy-matrix composites by dielectrophoretic force. *Advanced Materials Research*, 538–541: 2224–2231, 2012.

[11] S.U. Khan, J.R. Pothnis, J.-K. Kim, Effects of carbon nanotube alignment on electrical and mechanical properties of epoxy nanocomposites, *Composites Part A: Applied Science and Manufacturing*, 49: 26–34, 2013.

[12] H. Morgan, and N.G. Green. *AC electrokinetics: colloids and nanoparticles.* Research Studies Press, 2003.

[13] C. Park, J. Wilkinson, S. Banda, Z. Ounaies, K. Wise, G. Sauti, P. T. Lillehei, J. S. Harrison, Aligned single-wall carbon nanotube polymer composites using an electric field, *Journal of Polymer Science: Part B: Polymer Physics*, 44 : 1751-1762, 2006.

[14] Y. Liu, J.H. Chung, W.K. Liu, and R.S. Ruoff, Dielectrophoretic assembly of nanowires. *Journal of Physical Chemistry B*, 110(29):14098–14106, 2006.

[15] R. H. M. Chan, C.K.M. Fung, and W.J. Li, Rapid assembly of carbon nanotubes for nanosensing by dielectrophoretic force. *Nanotechnology*, 15(10) : S672– S677, 2004.

[16] T.B. Jones. *Electromechanics of particles*. Cambridge University Press, 2005.

[17] J. Cha , G. H. Jun , J. K. Park , J. C. Kim, H. J. Ryu, and S. H. Hong, Improvement of modulus, strength and fracture toughness of CNT/ Epoxy nanocomposites through the functionalization of carbon nanotubes, *Composites Part B: Engineering*, 129: 169-179, 2017.