Hierarchical Composite Structures Prepared by Electrophoretic Deposition of Carbon Nanotubes onto Glass Fibers

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SUPPLEMENTARY DATA

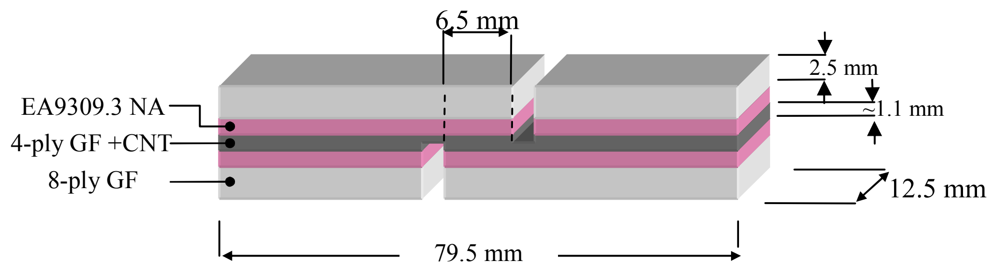

Figure S1. The configuration and dimensions of the test specimen used for measuring the in-plane shear strength of the CNT treated E-glass fiber. The 4-ply MWCNT treated laminate was bonded to two thicker outer laminates using EA9309.3NA adhesive.

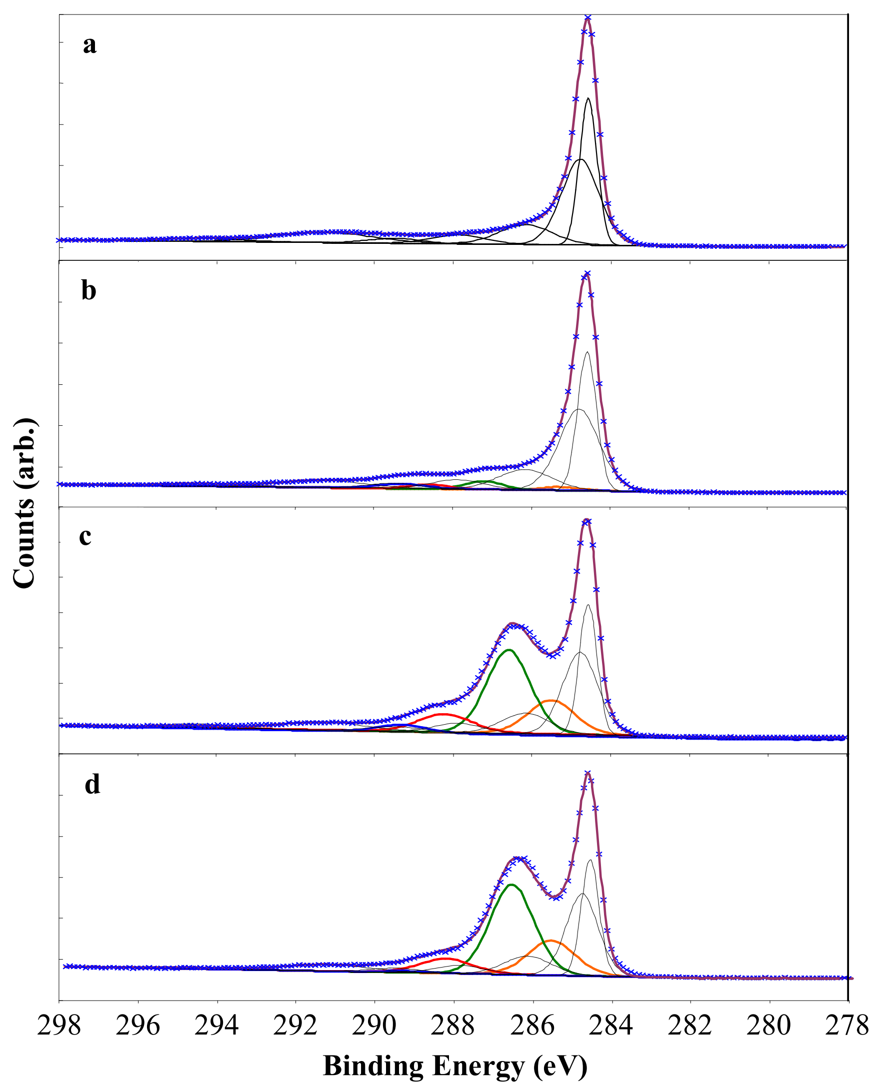

Figure S2. C 1s photolectron sprectra for (a) untreated CNTs, (b) ozone treated CNTs, (c) ozone and PEI treated CNTs and (d) ozone, PEI and GPS treated CNTs

Table S1. C 1s peak-fitting components as shown in Figure S1 for CNTs functionalized using ozone, PEI and GPS treatments

Sample	Atomic Concentration (%)					
Binding Energy (eV)	284.6	285.3-285.5	286.5-287.2	288.2-288.6	289.0-289.3	291.3
Component	Graphite	C-C	C-O/ C-N	C=O/ C=N	O-C=O/ O-C=N	π→π*
CNT	85.60	0.00	0.00	0.00	0.00	14.03
CNT-OZONE	71.89	1.18	2.85	1.56	2.09	7.47
CNT-OZONE-PEI	36.08	8.39	19.23	5.13	0.78	4.36
CNT-OZONE-PEI-GPS	34.44	9.13	21.90	4.39	0.38	3.48

Table S2. N 1s peak-fitting components for E-glass fabric before and after EPD with deionized water, PEI and GPS and CNTs functionalized using ozone, PEI

Sample	Atomic Concentration (%)				
Binding Energy (eV)	398.0	398.9	399.8-400.1	400.9-401.5	402.1-402.5
H_2O EPD of E-GLASS			1.6	0.8	1.1
PEI EPD of E-glass		6.0	1.7	1.0	
EPD of CNT-OZONE-PEI	1.0		8.6	2.6	1.7

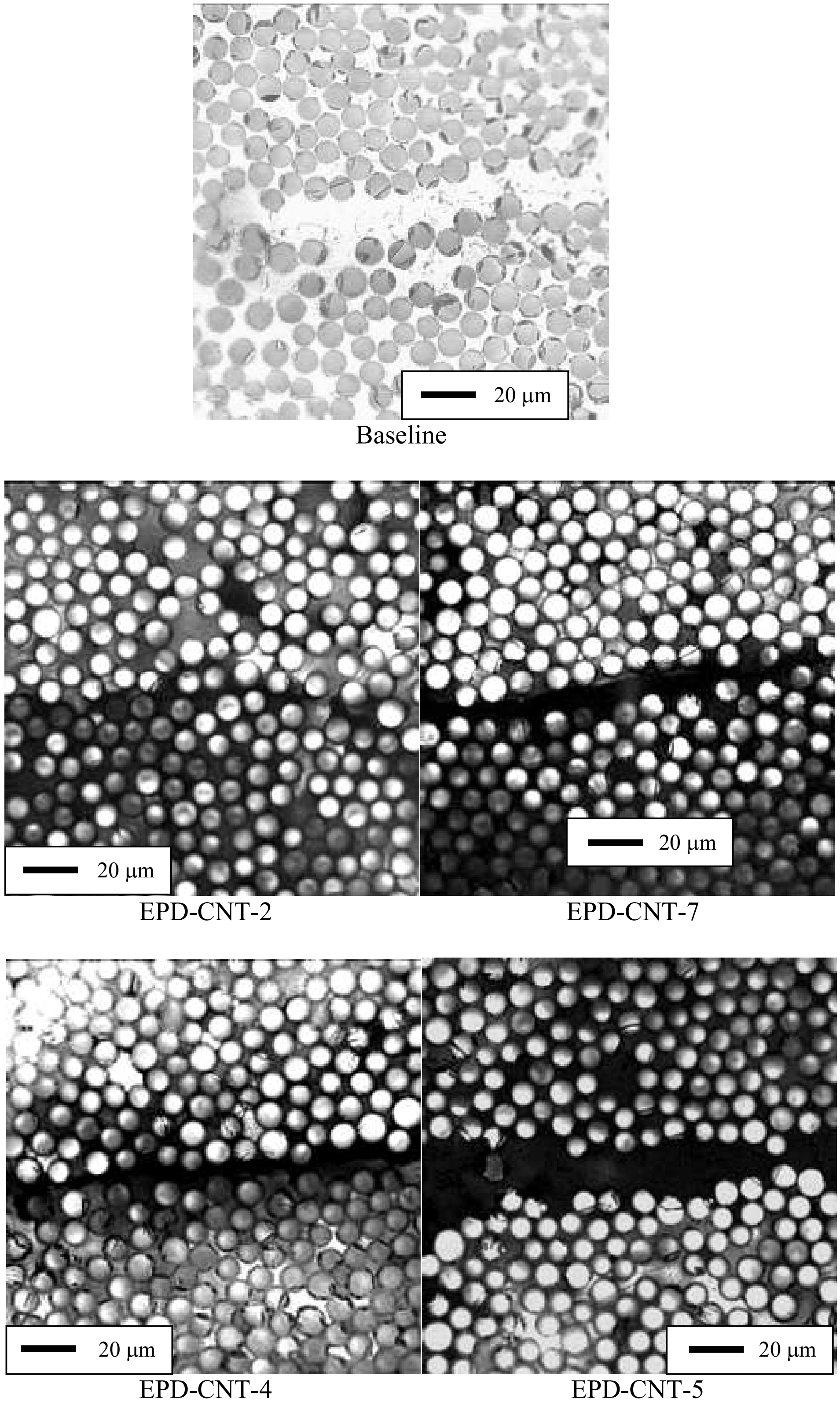

Figure S3. Optical images acquired using transmitted light for thin cross-sections of in-plane shear specimens indicating the interlaminar resin rich region and coating distribution through the laminate thickness

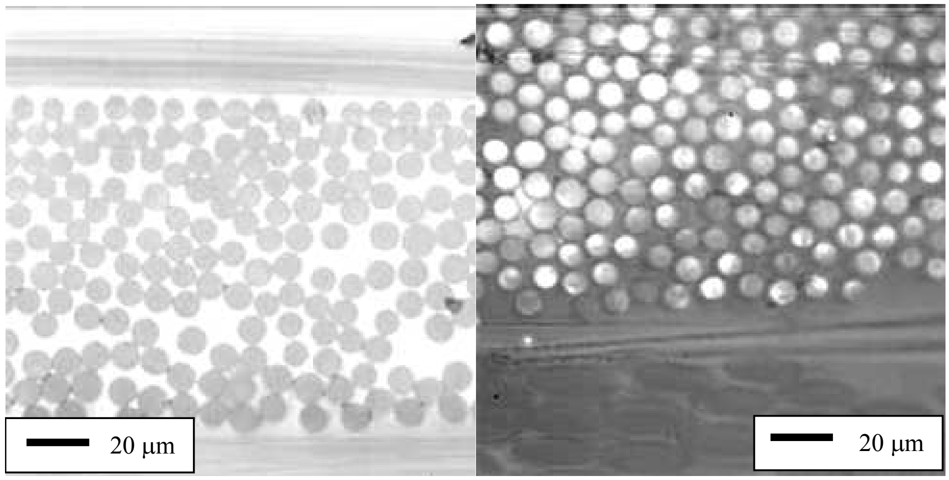

Figure S4. Optical images acquired using transmitted light for thin cross-sections of +/-45 shear specimens indicating the coating distribution through the laminate thickness compared to untreated laminate

Halpin-Tsai and Periodic Microstructure Model Equations Used for Modeling Shear Modulus of CNT Treated E-glass/Epoxy Laminates

The in-plane shear modulus, G_{12}, was estimated using the periodic microstructure model [S1], equation (S1):

$$G_{12} = G_m \left[1 + \frac{v_f (1 - G_m / G_f)}{G_m / G_f + S_3 (1 - G_m / G_f} \right] \qquad \text{(S1)}$$

Where v_f is the fiber volume fraction, G_m in the shear modulus of the epoxy matrix and G_f is the shear modulus of the E-glass fiber and S_3 is determined from equation (S2)

$$S_3 = 0.49247 - 0.47603 v_f - 0.05748 v_f^2 \qquad \text{(S2)}$$

In order to calculate the shear modulus of the matrix, it was assumed that the CNT coating present on the fibers was a constituent of the matrix. The CNTs were assumed to be present as a 3-D randomly oriented fibers in the epoxy matrix and G_{random} was estimated from equation (S3)[S2].

$$G_{random} = \frac{1}{8} E_{11} + \frac{1}{4} E_{22} \qquad \text{(S3)}$$

Where E_{11} and E_{22} are the tensile moduli in the principal and transverse fiber directions, respectively. E_{11} was calculated using equation (S4):

$$E_{11} = \frac{1 + 2(\frac{l_f}{d_f}) \eta_L v_f}{1 - \eta_L v_f} E_m \qquad \text{(S4)}$$

Where l_f and d_f are the CNT length and diameter, respectively, E_m is the tensile modulus of the matrix and η_L was determined from equation (S5):

$$\eta_L = \frac{(\frac{\alpha E_f}{E_m}) - 1}{(\frac{\alpha E_f}{E_m}) + 2(\frac{l_f}{d_f})} \tag{S5}$$

Where α is an orientation factor equal to 1/6 for the case where the CNT dimensions are significantly smaller than the laminate thickness [S3].

E_{22} was calculated using equation (S6):

$$E_{22} = \frac{1 + 2\eta_T v_f}{1 - \eta_T v_f} E_m \tag{S6}$$

Where η_T was determined from equation (S7):

$$\eta_T = \frac{(\frac{\alpha E_f}{E_m}) - 1}{(\frac{\alpha E_f}{E_m}) + 2} \tag{S7}$$

Table S3. Material property data used for modeling E-glass/epoxy shear modulus

Material Property	CNTs	Epon 862/Epikure W	E-glass
Tensile Modulus E (GPa)	200	2.72	72.4
Poisson ratio (υ)	---	0.33	0.22
Shear Modulus G (GPa)	---	1.02	29.7
Density ($g.cm^{-3}$)	2.0	1.2	2.55

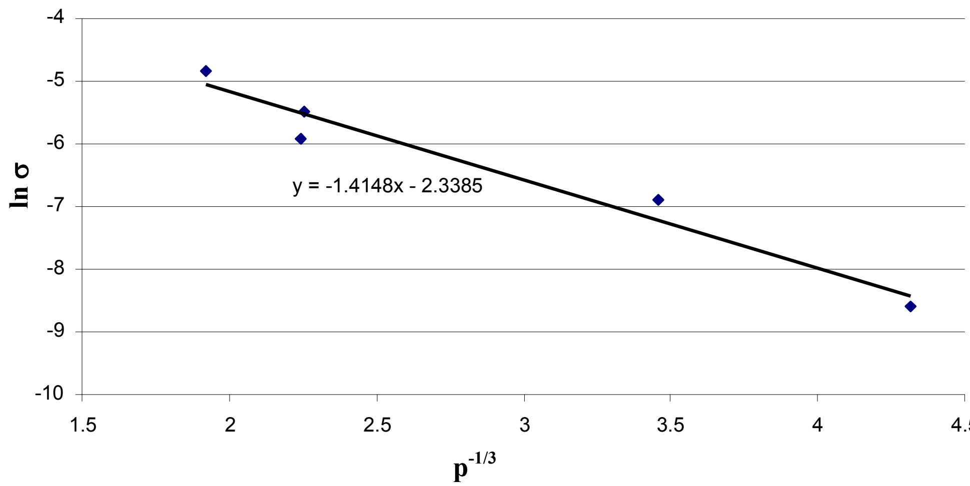

Figure S5. Plot of ln σ vs. $p^{-1/3}$ for CNT treated E-glass/epoxy laminates indicating a linear trend indicative of quantum tunnelling

REFERENCES

(S1) Luciano, R.; Barbero, E. J. *Int. J. Solids Struct.* **1994**, 31, 2933-2944

(S2) Halpin, J. C. *J Compos Mater* **1969**, 3, 732–734.

(S3) Yeh, M. –K.; Tai, N. –H.; Liu, J. –H. *Carbon* **2006**, 44, 1-9.