Supplementary information for:

Fabrication of Highly Tough, Strong, and Stiff Carbon Nanotube/Epoxy Conductive Composite with an Ultralow Percolation Threshold via Self-Assembly

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S1. Synthesis of tung oil based diglycidyl ester (TODGE)

S1.1. Materials

Methyl esters of tung oil fatty acids (TMA) was obtained from the Institute of Chemical Industry of Forestry Products Co., Ltd. (Nanjing, China), which contained about 85% conjugated methyl eleostearate.[1] Epichlorohydrin (> 99%), ethanol (> 99%), sodium hydroxide (> 99%), acrylic acid (> 99%), benzyltriethylammonium chloride (98%) were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd.

S1.2. TODGE synthesis

The scheme for TODGE preparation is shown in Fig. S1. Firstly, eleostearic acid (EA) was prepared and purified.[2] In a 1000 mL three-neck flask, ethyl alcohol (500 mL), distilled water (50 mL), and sodium hydroxide (44 g) were mixed together. When the temperature reached 75 °C, 292 g of TMA was dropped into the sodium hydroxide solution. After finishing dropping, the reaction was continued for 2h at 75 °C. After cooling, 5 mol/L hydrochloric acid was dropped into the mixture until the pH decreased to 2-3. The mixture was washed to neutral with distilled water, which was removed through distillation under vacuum. The product was dissolved without further treatment in 1000 mL of 95% ethanol. This solution was kept for 24 h at -20 °C to promote the formation of acid crystals. The very light-colored crystals were filtered and washed with about 75 mL of cold 95% ethanol, followed by vacuum drying to prepare light colored and pured EA. Then, 278 g EA and 0.695 g hydroquinone were charged into three-neck flask in a nitrogen atmosphere. After temperature reached 160 °C, 80 g acrylic acid was dropped into the mixture. The reaction continued at that temperature for 5 h. The excess acrylic acid was removed by using a rotary evaporator under vacuum. Adduct of EA and acrylic acid (EAA) was obtained. Finally, EAA was reacted with epichlorohydrin to produce TODGE. 46.1 g EAA (0.1mol), 185 g epichlorohydrin (2 mol), and 0.455 g benzyltriethylammonium chloride (2 mmol) were added into 500 ml three-neck flask. The reaction temperature was raised to 117 °C and the reaction continued for 6 h. After the mixture was cooled to 60 °C, 20 g 40 wt% sodium hydroxide aqueous solution (sodium hydroxide: 8 g) were charged. The mixture was stirred at 60 °C for 3 h. After that, the solids were filtered and the excess epichlorophydrin in the filter liquid was distilled under vacuum for recycling. A yellowish viscous resin TODGE with an epoxide value of 0.35 equiv/100g (theory: 0.43 equiv/100g) was obtained.

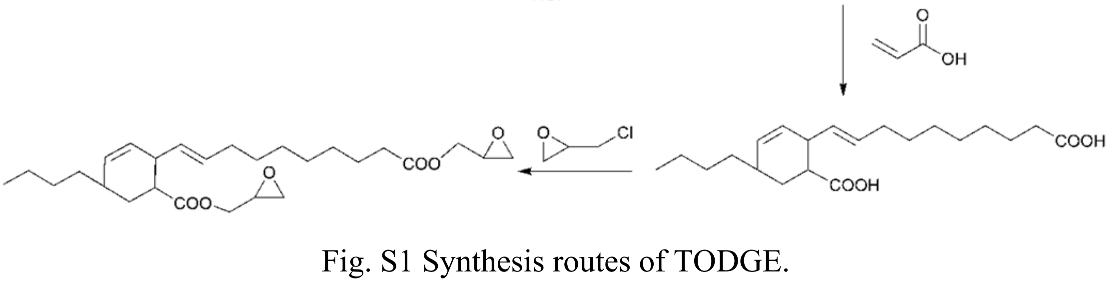

Fig. S1 Synthesis routes of TODGE.

S1.3. Characterization

Fourier transform infrared (FT-IR) analysis was performed on a Thermo Scientific Nicolet iS10 spectrometer. The ^{1}H and ^{13}C NMR spectra of the TODGE were conducted on a Bruker 400 MHz spectrometer (Bruker) at room temperature with a solvent of deuterated chloroform ($CDCl_3$).

S1.4. Results

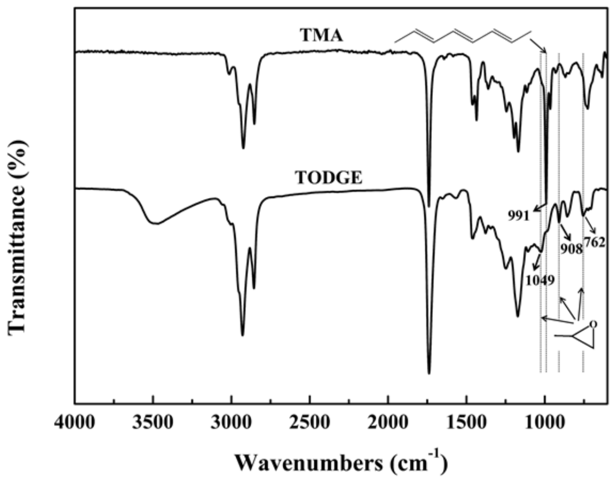

Fig. S2 FTIR spectra of TMA and TODGE.

Fig. S2 is the FTIR spectra of TMA and TODGE. The strong peak at 991 cm^{-1} is attributed to the conjugated double bonds of TMA. For TODGE, the peak is disappeared, indicating that TMA has already reacted with acrylic acid after the reaction. Meanwhile, the characteristic peaks of the epoxy (762, 908, and 1049 cm^{-1}) are appeared. Therefore, after reaction, TODGE is successfully synthesized.

Fig. S3 and Fig. S4 are the ^{1}H and ^{13}C NMR spectrum of TODGE. The chemical shift assignments are also labeled in the figures. From the figures, it is also proved that the TODGE is successfully synthesized.

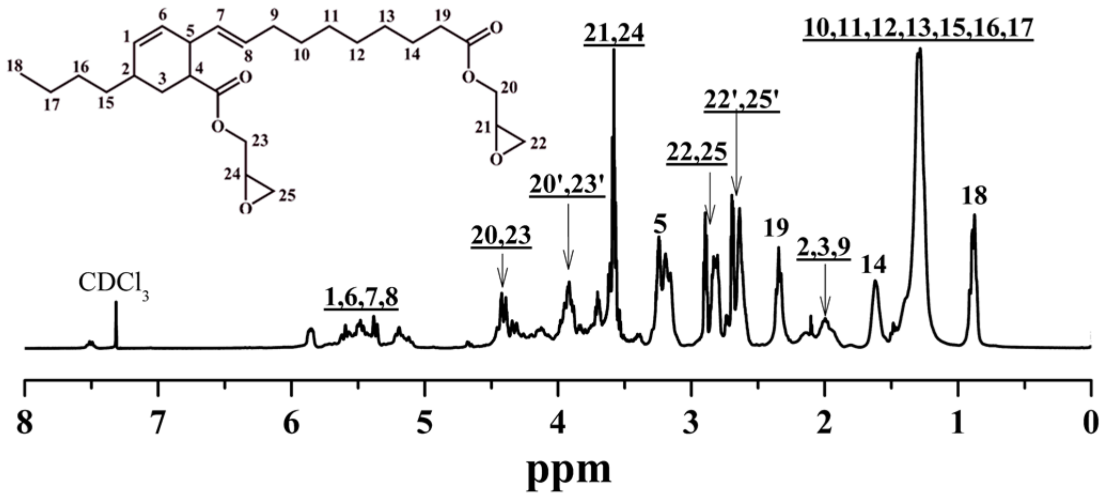

Fig. S3 ^{1}H NMR spectrum of TODGE.

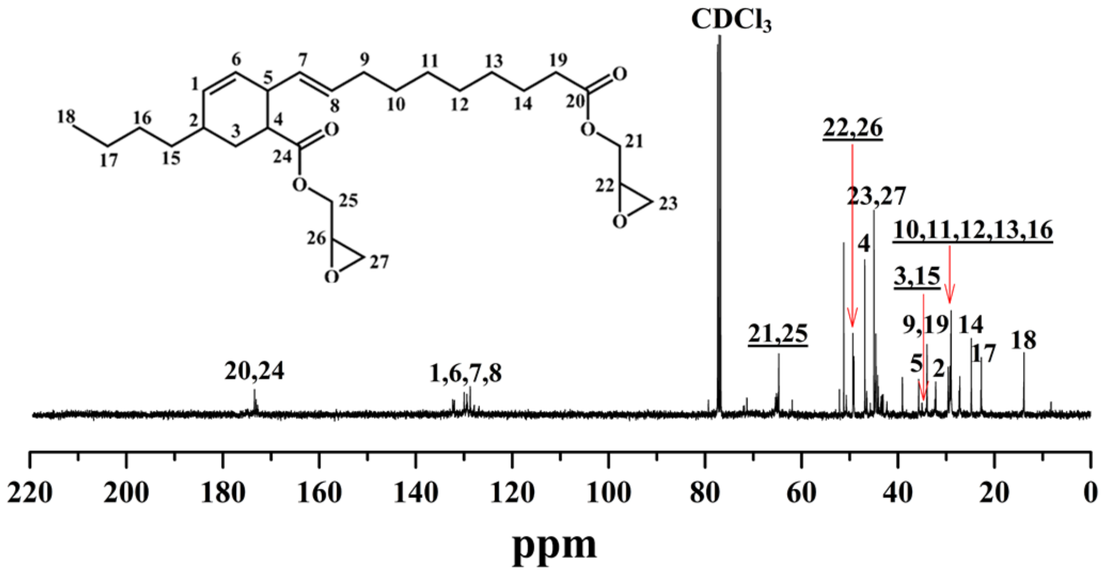

Fig. S4 ^{13}C NMR spectrum of TODGE.

S2. Fabrication details of 0.25 wt% MWCNT/DGEBA/TODGE epoxy composites with different weight ratios of DGEBA/TODGE

Table S1 Fabrication details of 0.25 wt% MWCNT/DGEBA/TODGE epoxy composites with different weight ratios of DGEBA/TODGE

Weight ratio of DGEBA/ TODGE	Epoxide value of epoxy resin (equiv./100g)	Weight ratio of POP-D400/ epoxy resin	TODGE content (wt%)	DGEBA content (wt%)	MWCNT content in DGEBA domain (wt%)
100:0	0.51	0.55	0	64.35	0.39
90:10	0.51	0.55	6.44	57.92	0.43
80:20	0.47	0.50	13.30	53.20	0.47
70:30	0.46	0.50	19.95	46.55	0.53
60:40	0.44	0.45	27.52	41.28	0.60
50:50	0.42	0.45	34.40	34.40	0.72
30:70	0.38	0.40	49.87	21.37	1.15

S3. Measurement of interfacial energy between MWCNT and epoxy i

The interfacial energy between two components γ_{12} can be calculated according to the harmonic-mean equation:

$$\gamma_{12}=\gamma_1+\gamma_2-4\left(\frac{\gamma_1^{d}\gamma_2^{d}}{\gamma_1^{d}+\gamma_2^{d}}+\frac{\gamma_1^{p}\gamma_2^{p}}{\gamma_1^{p}+\gamma_2^{p}}\right) \quad (1)$$

or geometric-mean equation:

$$\gamma_{12}=\gamma_1+\gamma_2-2\left(\sqrt{\gamma_1^{d}\gamma_2^{d}}+\sqrt{\gamma_1^{p}\gamma_2^{p}}\right) \quad (2)$$

where γ_i is the surface energy of component i, γ_i^{d} is the dispersive part of the surface energy of component i, and γ_i^{p} is the polar part of the surface energy of component i. The surface energy γ_i, which is the sum of γ_i^{d} and γ_i^{p}, can be calculated from the measurement of contact angle θ. Before measurement, the uncured DGEBA and TODGE were coated on a glass slide. Contact angle measurements were performed with a DSA100 apparatus (Kruss Co Ltd., Germany) at room temperature. The contact angle measurement of a certain epoxy was carried out at least 5 times and the average results were provided. The relationship between θ and γ_i can be described by the Owens-Wendt method:[3]

$$\gamma_l(1+\cos\theta)=2(\sqrt{\gamma_i^d\gamma_l^d}+\sqrt{\gamma_i^p\gamma_l^p}) \quad (3)$$

where γ_l is the surface energy of liquid, γ_l^d is the dispersive part of the surface energy of liquid, and γ_l^p is the polar part of the surface energy of liquid. In the current study, H_2O and CH_2I_2 are selected as probe liquids. The surface energy data of H_2O and CH_2I_2 are $\gamma_{H_2O}^d$ = 21.8 dyn·cm^{-1}, $\gamma_{H_2O}^p$ = 51.0 dyn·cm^{-1}, $\gamma_{CH_2I_2}^d$ = 49.5 dyn·cm^{-1}, and $\gamma_{CH_2I_2}^p$ = 1.3 dyn·cm^{-1}.[3] The contact angles of H_2O on the surfaces of DGEBA and TODGE are 53.4°, and 15.3°, respectively. The contact angles of CH_2I_2 on the surfaces of DGEBA and TODGE are 11.2° and 7.9°, respectively. The surface energies of DGEBA and TODGE are calculated according to equation (3) and the results are listed in the Table S2. For MWCNTs, the parameter (γ: 27.8 mJ·m^{-2}, γ^d: 17.6 mJ·m^{-2}, γ^p: 10.2 mJ·m^{-2}) is selected because MWCNTs are produced by the chemical vapor deposition method.[4, 5] The interfacial energies between different components are then calculated according to equations (1) and (2), and the results are shown in Table S3.

Table S2 The surface energy data of components

Components	γ^{d} (mJ·m^{-2})	γ^{p} (mJ·m^{-2})	γ (mJ·m^{-2})
DGEBA	42.6	15.0	57.6
TODGE	38.7	35.3	74.0
MWCNT[a]	17.6	10.2	27.8

[a] According to Barber et al.[5]

Table S3 Interfacial energies γ_{12} between different components calculated from harmonic and geometric mean equations

Component couple	γ_{12} (mJ·m^{-2})	
	Based on the harmonic mean equation	Based on the geometric mean equation
MWCNT/DGEBA	11.3	5.9
MWCNT/TODGE	21.8	11.7

S4. Mechanical properties of the composites and SEM characterization of MWCNT powder and cross-sectional fracture surfaces of the composites

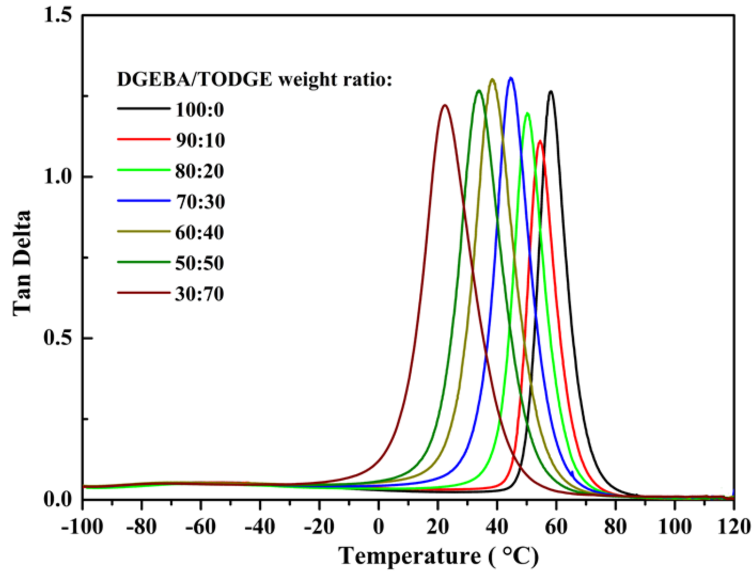

Fig. S5 Temperature dependence of loss factor tanδ for 0.25 wt% MWCNT/DGEBA/TODGE epoxy composites with different DGEBA/TODGE weight ratios.

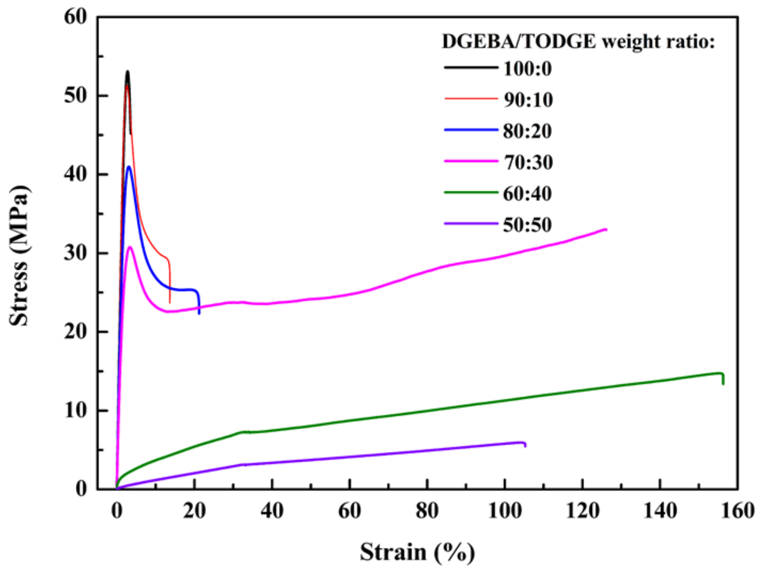

Fig. S6 Stress−strain curves of 0.25 wt% MWCNT/DGEBA/TODGE epoxy composites with different DGEBA/TODGE weight ratios.

Table S4 Tensile properties of 0.25 wt% MWCNT/DGEBA/TODGE epoxy composites with different DGEBA/TODGE weight ratios

Weight ratio of DGEBA/ TODGE	Tensile strength σ_b (MPa)	Elongation at break ε_b (%)	Young's modulus E (MPa)	Toughness T^a (MJ/m^3)
100:0	53.81 ± 0.91	3.98 ± 0.38	2920.32 ± 111.08	167.02 ± 14.51
90:10	50.87 ± 0.33	13.00 ± 0.97	2813.45 ± 129.40	459.69 ± 28.94
80:20	41.17 ± 0.40	21.18 ± 3.74	2677.50 ± 64.28	579.93 ± 94.62
70:30	30.95 ± 1.91	118.91 ± 5.29	2159.95 ± 117.69	2731.62 ± 310.34
60:40	14.76 ± 0.82	157.98 ± 4.16	140.08 ± 61.67	1557.25 ± 116.48
50:50	5.81 ± 0.26	106.10 ± 4.14	8.89 ± 0.79	373.05 ± 44.80

[a] The value is calculated by integrating the area under stress−strain curves.

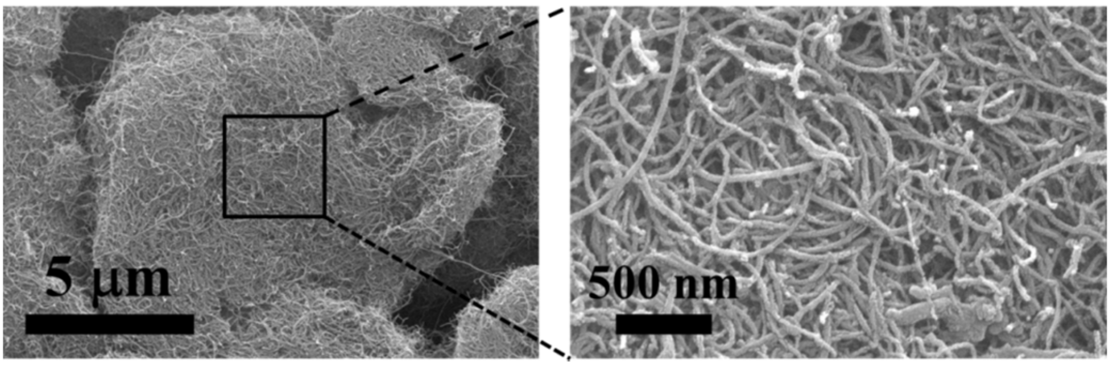

Fig. S7 SEM images of MWCNTs' powder.

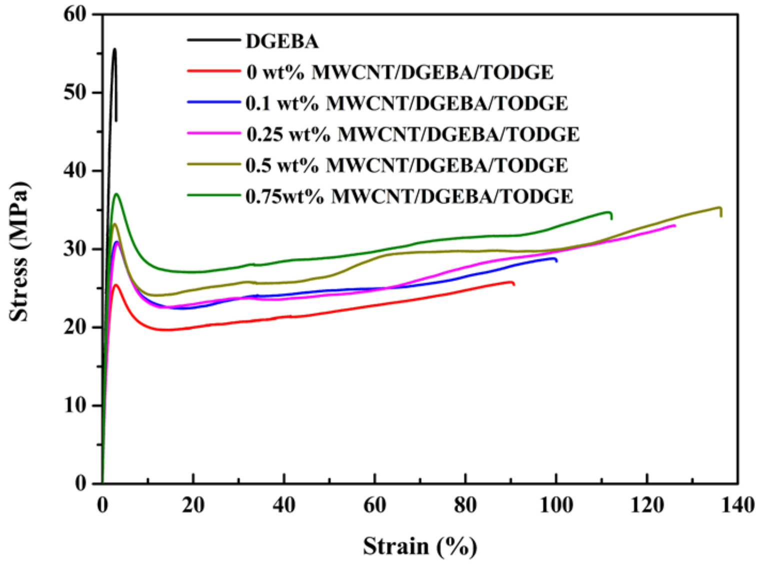

Fig. S8 Stress−strain curves of neat DGEBA epoxy and MWCNT/DGEBA/TODGE epoxy composites (DGEBA/TODGE = 70w/30w) with different MWCNT contents.

Table S5 Tensile properties of the neat DGEBA epoxy resin and MWCNT/DGEBA/TODGE epoxy composites (DGEBA/TODGE = 70w/30w) with different MWCNT contents

MWCNT content (wt%)	Tensile strength σ_b (MPa)	Elongation at break ε_b (%)	Young's modulus E (MPa)	Toughness T^a (MJ/m^3)
DGEBA	53.40 ± 2.19	3.23 ± 0.25	2893.84 ± 36.30	116.76 ± 7.84
0	25.85 ± 1.32	99.32 ± 14.19	1928.60 ± 249.43	2214.59 ± 305.50
0.1	29.97 ± 0.72	108.26 ± 8.04	1974.09 ± 102.80	2511.57 ± 74.48
0.25	30.95 ± 1.91	118.91 ± 5.29	2159.95 ± 117.69	2731.62 ± 310.34
0.5	34.74 ± 1.32	126.09 ± 13.50	2559.58 ± 194.78	3692.05 ± 544.96
0.75	37.09 ± 1.28	112.84 ± 4.25	2881.99 ± 140.56	3249.98 ± 117.74

[a] The value is calculated by integrating the area under stress−strain curves.

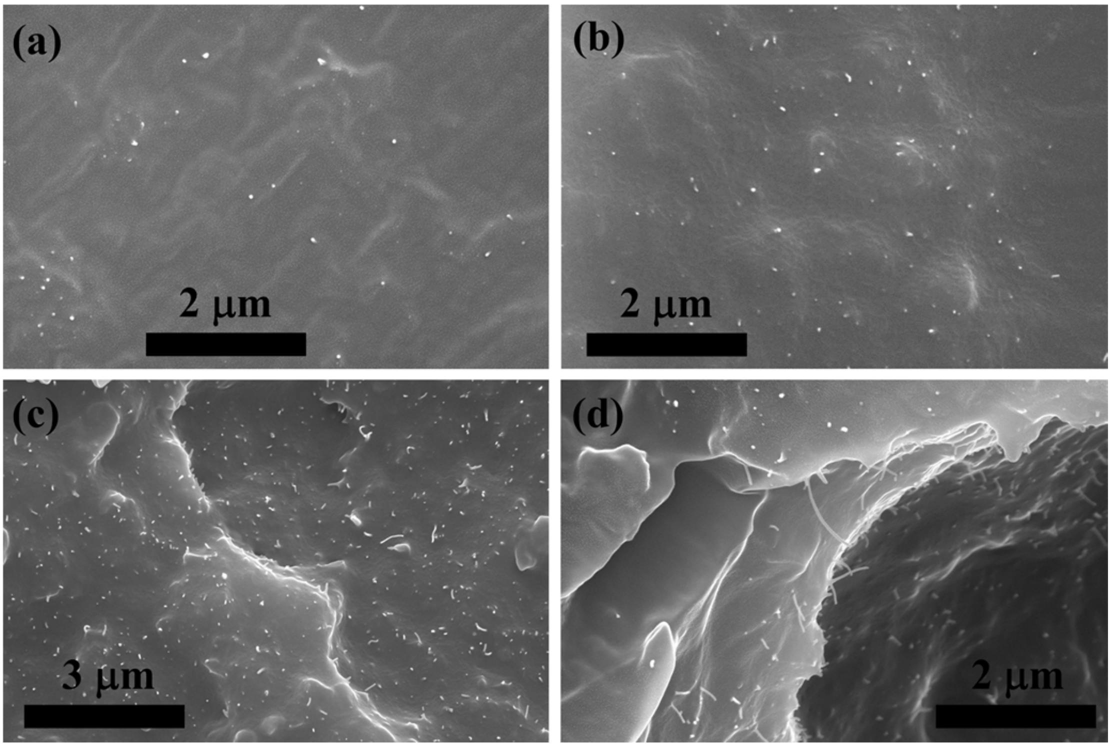

Fig. S9 SEM images of cross-sectional fracture surfaces of MWCNT/DGEBA/TODGE (DGEBA/TODGE = 70w/30w) epoxy composites with different MWCNT contents: (a) 0.1 wt%, (b) 0.25 wt%, (c) 0.5 wt%, (d) 0.75 wt%.

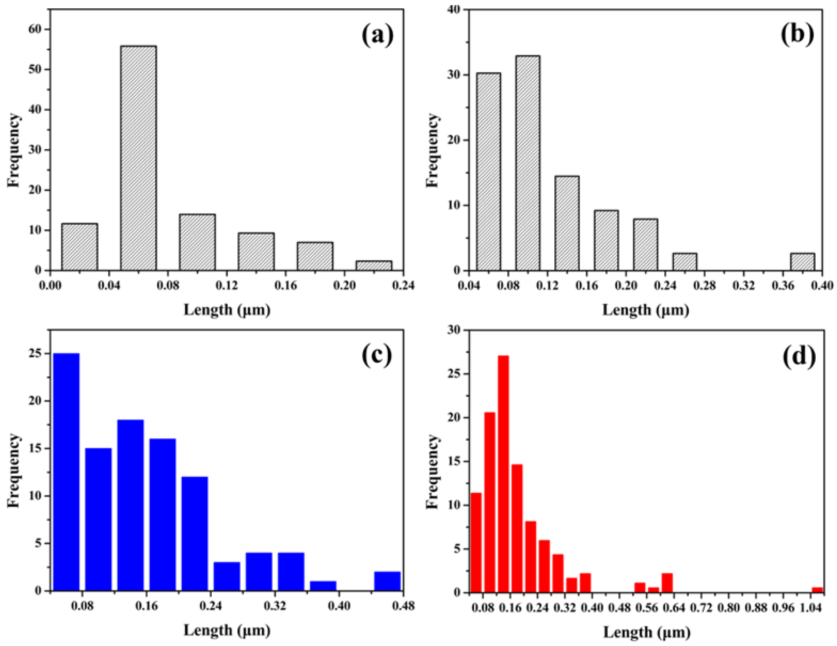

Fig. S10 Histograms of the length distribution of residual MWCNT on the tensile fracture surfaces of MWCNT/DGEBA/TODGE (DGEBA/TODGE = 70w/30w) epoxy composites with different MWCNT contents: (a) 0.1 wt%, (b) 0.25 wt%, (c) 0.5 wt%, (d) 0.75 wt%. The length measurement of MWCNTs is performed by using a semi-automatic digital image analysis software Image J (NIH, USA).

Table S6 Statistics about the length of residual MWCNT on the tensile fracture surfaces of MWCNT/DGEBA/TODGE epoxy composites (DGEBA/TODGE = 70w/30w) with different MWCNT contents

MWCNT content (wt%)	Mean (μm)	Minimum (μm)	Maximum (μm)
0.10	0.078	0.024	0.22
0.25	0.12	0.051	0.37
0.50	0.16	0.050	0.48
0.75	0.18	0.051	1.08

References

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