

Functionalized Carbon-Nanotube Sheet/Bismaleimide Nanocomposites: Mechanical and Electrical Performance Beyond Carbon-Fiber Composites

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Since their discovery in 1991, carbon nanotubes (CNTs) have been considered as the next-generation reinforcement materials to potentially replace conventional carbon fibers for producing super-high-performance lightweight composites. Herein, it is reported that sheets of millimeter-long multi-walled CNTs with stretch alignment and epoxidation functionalization reinforce bismaleimide resin, which results in composites with an unprecedentedly high tensile strength of 3081 MPa and modulus of 350 GPa, well exceeding those of state-of-the-art unidirectional carbon-fiber-reinforced composites. The results also provide important experimental evidence of the impact of functionalization and the effect of alignment reported previously on the mechanical performance and electrical conductivity of the nanocomposites.

Keywords:

- carbon nanotubes
- conductivity
- functionalization
- mechanical properties
- nanocomposites

1. Introduction

Bismaleimide (BMI) resin/carbon-nanotube (CNT) composites are very attractive for high-temperature and high-conductivity applications. BMI resins are widely used as a polymeric matrix for high-temperature and -performance carbon-fiber-composite applications due to their high glass transition temperature, excellent thermal stability, and good epoxy-like processability for composite fabrication. Since their discovery in 1991,^[1] CNTs have been considered the most promising candidate as the next generation of reinforcement material for developing multifunctional and high-performance lightweight composites. Several researchers report attempting to reinforce BMI resin with CNTs;^[2,3] however, the resultant mechanical properties were much lower than the predicted values due to several obstacles, such as low CNT loading, poor

interfacial bonding, short CNT length, and lack of nanotube alignment.

Herein, we report the functionalization of CNT sheets to reinforce BMI composites that demonstrate mechanical properties beyond those of state-of-the-art aerospace-grade unidirectional carbon-fiber composites for structural applications. The mechanical properties of the resultant CNT-sheet/BMI composites were normalized to 60 vol% nanotube volume content and compared with those of unidirectional carbon-fiber composites.^[4,5] As shown in Figure 1, after epoxidation functionalization, the mechanical properties of functionalized 40% stretch alignment CNT-sheet^[6]/BMI composites were dramatically improved compared to unfunctionalized samples. The Young's modulus exceeded that of high-modulus carbon-fiber composites, such as M60J epoxy composite, and the tensile strength was 15–20% higher than that of high-strength T1000G epoxy composites. The major factors in realizing such ultrahigh properties are the improvements in both interfacial bonding and degree of alignment of the CNTs.

In a previous report,^[6] we demonstrated that the degree of alignment of the CNTs is critical for improving the mechanical properties of the resultant CNT-sheet/BMI composites, when using commercially available CNT sheets of millimeter-long nanotubes.^[7] The effects of alignment degree and the high concentration of CNTs on the mechanical properties were revealed. We achieved an 80% degree of CNT alignment in the 40% stretch samples. However, we also observed substantial

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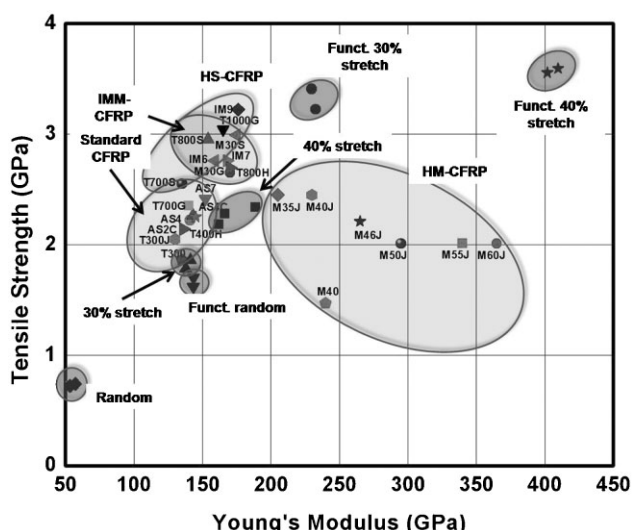


Figure 1. Comparison of tensile strength and modulus of the CNT-sheet/BMI composites with those of unidirectional carbon-fiber-reinforced polymer composites (CFRP) with 60% carbon fiber or CNT volume fraction contents, which show exceptional integration of high strength, high modulus, and large failure strain beyond those of current CFRP systems. IMM-CFRP: immediate-modulus CFRP; HS-CFRP: high-strength CFRP; HM-CFRP: high-modulus CFRP.

nanotube pullouts and no nanotube breaks at the fracture surface, which implies weak interfacial bonding. Herein, we report a follow-up effort to improve the interfacial bonding through epoxidation functionalization. We studied the reaction mechanism of the functionalized CNTs and BMI resin to form covalent bonds. The combination of stretch alignment and epoxidation functionalization of CNT sheets is a unique approach to overcome the major obstacles for developing high-performance nanocomposites, which are a long-standing anticipation for both the academic community and industry.

2. Results and Discussion

The resin system used in this study was Cytec's BMI 5250-4 resin, which contains three components.^[8,9] 4,4'-bismaleimidediphenylmethane, *o,o'*-diallyl bisphenol A, and BMI-1,3-tolyl (see Figure S1 in the Supporting Information). According to a phenol-epoxy curing mechanism,^[10] active epoxy groups can react with hydroxyl groups of *o,o'*-diallyl bisphenol A. Hence, we can utilize epoxide-functionalized CNTs to realize covalent bonding with BMI resin matrices. This functionalization method is relatively simple for tailoring the degree of functionalization under gentle reaction conditions to avoid damage to the preformed nanotube alignment and structural integrity of the sheet.^[11]

Recently, researchers^[12] used peroxide acid (*m*-chloroperoxybenzoic acid or *m*-CPBA, see Figure S1 in the Supporting Information) to treat single-walled carbon nanotubes (SWNTs) and successfully introduced an epoxy ring on the structure of the SWNTs. In this study, we used this method to functionalize both randomly dispersed and aligned CNT sheets under very low concentrations of *m*-CPBA to realize a tailored 4% degree of functionalization, to minimize damage to the CNT structure and

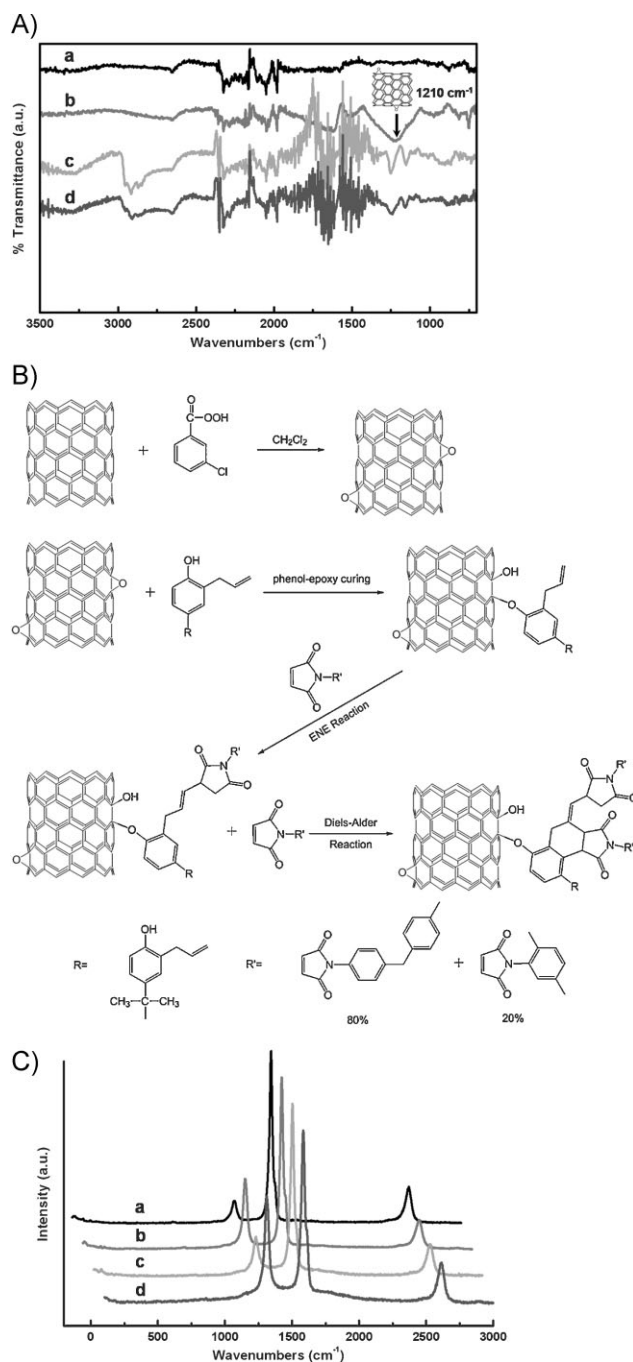


Figure 2. A) Comparison of ATR-FTIR spectra: a) pristine CNT, b) epoxidation-functionalized CNT, and c) pristine and d) functionalized 40% stretch alignment CNT-sheet/BMI nanocomposites. B) Proposed reaction mechanism of functionalized CNTs and BMI 5250-4 resin. C) Comparison of Raman spectra: a) pristine CNTs, b) functionalized CNTs, c) pristine 40% stretch alignment CNT-sheet/BMI composite, and d) functionalized 40% stretch alignment CNT-sheet/BMI composite.

degradation of the mechanical properties of the composite.^[11] Figure 2A shows attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectra of pristine CNTs, functionalized CNTs, and aligned (40% stretch) pristine and functionalized CNT-sheet/BMI composites. The peak at 1210 cm⁻¹ is attributed to epoxide ring groups,^[12] which confirms that the epoxide group was successfully attached to the CNT structure.

After curing with BMI resin (see trace d, Figure 2A), the peak at 1210 cm^{-1} disappeared, which indicates that the epoxide ring groups reacted with the BMI resin. The FTIR spectrum of the pristine-CNT-sheet/BMI composite is shown in trace c. Both FTIR spectra were almost the same, which further confirms that the epoxide rings on the CNT structures reacted to form covalent bonds with the BMI resin matrix.

Figure 2B shows the proposed reaction mechanism. The epoxide groups of functionalized CNTs first reacted with *o,o'*-diallyl bisphenol A in accordance with the mechanism of the epoxy-phenol reaction.^[10] Then, the derivative reacted with the other two BMI components to form three-dimensional crosslinked structures through ene and Diels-Alder reactions.^[8,9] The formation of carbon-oxygen bonds between CNTs and the BMI resin dramatically enhanced the interfacial bonding, and hence the load transfer efficiency was improved after functionalization.

We also studied the proposed curing mechanism by Raman spectroscopy. The intensity ratio of the disorder band (D band at $\approx 1310\text{ cm}^{-1}$) with the G band ($\approx 1580\text{ cm}^{-1}$) of the functionalized CNTs increased, which indicates the formation of epoxide rings on the structure of the CNTs (see Figure 2C). The R value (I_D/I_G) of pristine CNTs was 0.13. After functionalization, the I_D/I_G value increased to 0.41. In the pristine-CNT-sheet/BMI composite, the I_D/I_G value increased to 0.23 due to the coupling effect of the CNTs and BMI crosslinked structure. For the functionalized-CNT-sheet/BMI composite, the I_D/I_G further increased up to 0.62, which further indicates stronger

interactions, possibly due to the formation of chemical bonds between the functionalized CNTs and BMI resin.

Figure 3A shows typical stress-strain curves of CNT-sheet-reinforced BMI nanocomposites along the nanotube alignment direction. Figure 3B compares the detailed tensile strength and Young's modulus of the samples. Compared to the pristine random CNT-sheet-reinforced BMI nanocomposites, the tensile strength and Young's modulus of the pristine nanocomposites dramatically increased with the increase of alignment degree previously reported.^[6] After functionalization to introduce epoxide groups on the CNTs followed by covalent bonding with the BMI resin matrix, the mechanical properties of the resultant nanocomposites were further improved. The tensile strength and Young's modulus of functionalized random CNT-sheet/BMI nanocomposites reached 1437 MPa and 124 GPa, respectively, which are about two times greater than those of pristine random CNT-sheet/BMI nanocomposites previously reported.^[6] For functionalized 30% stretch alignment CNT-sheet/BMI nanocomposites, the tensile strength and Young's modulus reached up to 2843 MPa and 198 GPa, respectively, which is a 78% and 62% improvement over that of the pristine 30% stretch alignment CNT-sheet/BMI nanocomposites. For functionalized 40% stretch alignment CNT-sheet/BMI nanocomposites, the tensile strength and Young's modulus reached 3081 MPa and 350 GPa, respectively, which are 48% and 107% improvements over that of pristine 40% stretch CNT-sheet/BMI nanocomposites. However, the failure strains of functionalized-CNT-sheet/BMI

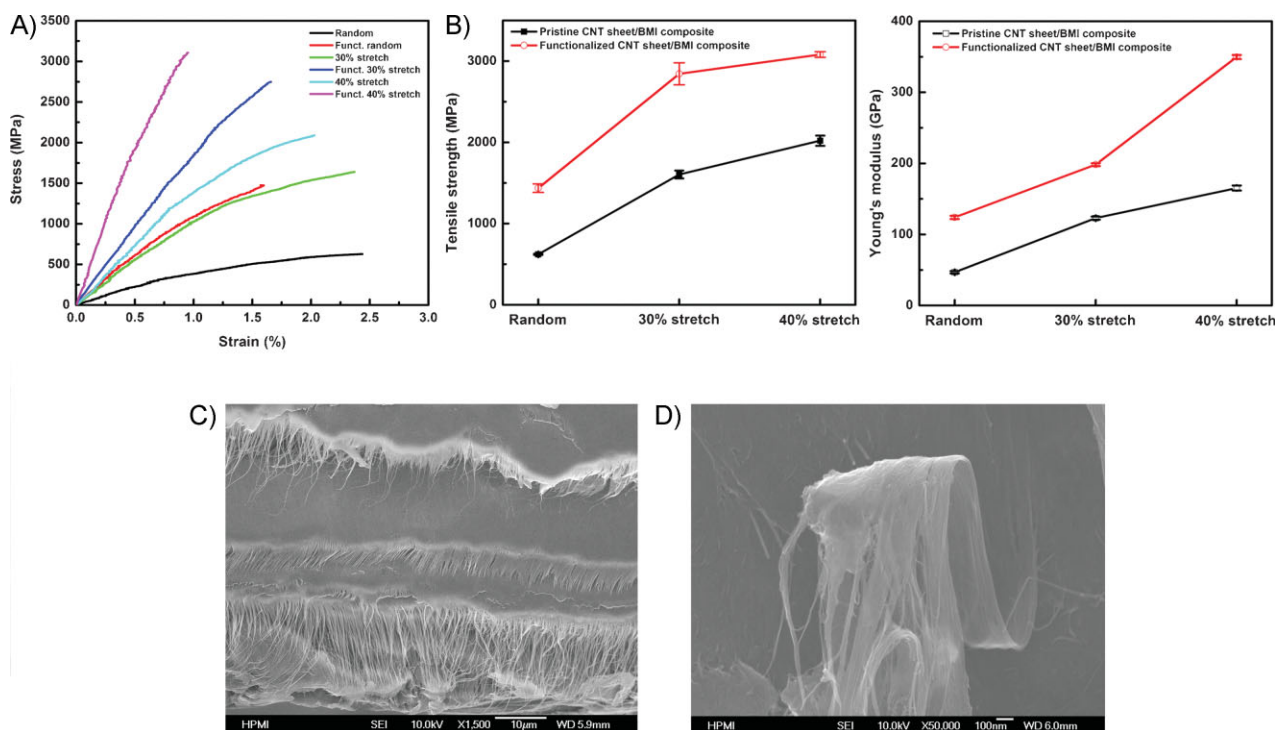


Figure 3. Exceptional mechanical performance of CNT-sheet/BMI composites. A) Typical tensile stress-strain curves of random and stretch-aligned CNT-sheet/BMI composites with and without functionalization, which illustrate a significant improvement of the mechanical properties through alignment and functionalization. B) Comparisons of tensile strength and Young's modulus measurements of the resultant composites with and without functionalization. C, D) Scanning electron microscopy images of the typical fracture surface morphology of functionalized-CNT-sheet/BMI composite with 40% stretch alignment.

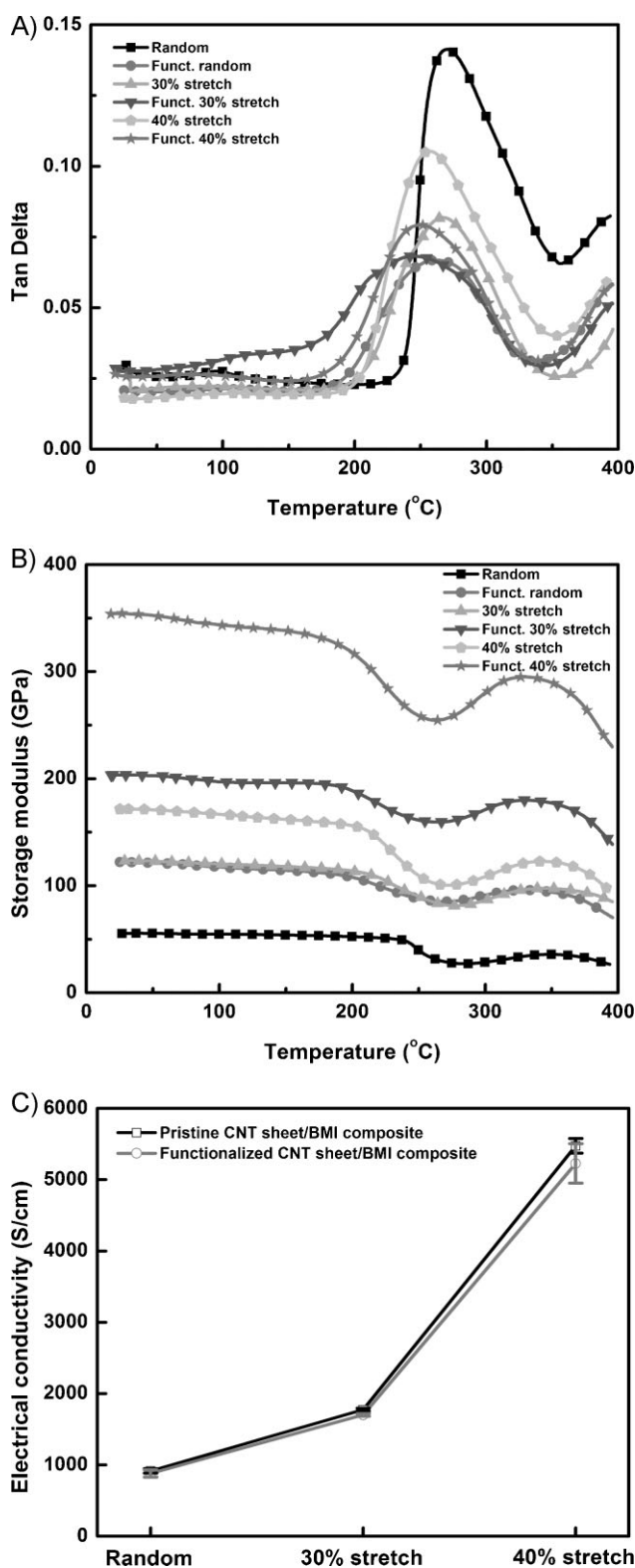


Figure 4. A) Comparisons of tan delta curves and B) storage moduli of the CNT-sheet/BMI composite with and without functionalization. C) Comparisons of electrical conductivity values parallel to the CNT alignment direction in the resultant composites.

nanocomposites decreased sharply (see Figure 3A). The failure strain of functionalized 40% stretch alignment CNT-sheet/BMI nanocomposites dropped to 0.95%. This effect has two possible reasons: 1) the formation of covalent bonds significantly reduced nanotube pullout and restricted the nanotube network deformation capability; and 2) possible nanotube structural damage due to functionalization resulted in a loss of a certain degree of ductility of the CNTs. Therefore, the degree of functionalization is a very important parameter that needs to be optimized to improve strength and modulus without sacrificing failure strain. Here, based on our experimental study,^[11] we tailored the degree of functionalization to 4% to minimize CNT damage and the reduction of the failure strain of the composites.

Figure 3C and D shows the fracture surface morphology of a functionalized 40% stretch alignment specimen after tensile testing. Rather than peeling off, as seen in the pristine-CNT-sheet/BMI samples previously reported,^[6] it can be clearly seen that the BMI resin and aligned CNT layers adhered very well due to good interfacial bonding. Although the interfacial bonding and load transfer efficiency were dramatically improved with this chemical functionalization, which resulted in the record high mechanical properties exceeding those of state-of-the-art aerospace-grade unidirectional carbon-fiber composites, many CNT slippage and pullout modes were still observed. Also, most of the nanotubes were not broken after tensile testing, which implies that the full potential of the CNTs' strength has yet to be achieved. Further improvement in the alignment and the optimization of functionalization and interfacial bonding could lead to greater performance.

Figure 4A and B shows dynamic mechanical analysis (DMA) results. Table 1 shows the storage modulus of the samples. The T_g values of all CNT-sheet/BMI composites dropped due to the introduction of high loading of CNTs, which possibly reduced the crosslink density of the BMI resin matrix. Compared with pristine-CNT-sheet/BMI composites, the T_g values of functionalized-CNT composites dropped further, which may be due to the epoxide groups of functionalized CNTs reacting and consuming some functional groups of the BMI resin, and hence further reducing the crosslink density.

Table 1. Comparison of storage modulus and glass transition temperature (T_g) of CNT-sheet/BMI composites with and without functionalization.

Specimen	Storage modulus [GPa]	T_g [°C]
Pristine random CNT sheet/BMI composite ^[6]	55	269.98
Functionalized random CNT sheet/BMI composite	122	262.67
Pristine 30% stretch CNT sheet/BMI composite ^[6]	123	266.77
Functionalized 30% stretch CNT sheet/BMI composite	203	241.80
Pristine 40% stretch CNT sheet/BMI composite ^[6]	172	256.70
Functionalized 40% stretch CNT sheet/BMI composite	354	247.44

However, the T_g drop of the functionalized-CNT/BMI composites was only 23 °C, and the composites still had a T_g of 247 °C for high-temperature applications. Another side effect of chemical functionalization of CNTs is degradation of their electrical conductivity. Usually, chemical functionalization will damage the original CNT electronic structure and lower the electrical conductivity.^[13] In this research, we tried to tailor the degree of functionalization to a lower level of 4%, to limit the electrical conductivity degradation. Figure 4C shows a comparison of the electrical conductivities of CNT-sheet/BMI composites with and without functionalization. The electrical conductivities of the functionalized-CNT composites only show a small reduction, less than 5%, due to the lower degree of functionalization.

3. Conclusions

In summary, we successfully introduced epoxide groups on CNT structures through epoxidation functionalization, and demonstrated the record high performance of the CNT-sheet/BMI composites, which was beyond that of state-of-the-art high-strength and high-modulus unidirectional carbon-fiber composites for structural applications. The reaction mechanism of functionalized CNTs with BMI is proposed. A limited effect of CNT functionalization on the T_g and electrical conductivity was observed due to a tailored low degree of functionalization. The results demonstrate great potential for utilizing CNTs to develop the next generation of high-performance composites for wide structural and multifunctional applications.

4. Experimental Section

Materials and fabrication of functionalized-CNT-sheet/BMI nanocomposite: Randomly oriented CNT sheets (supplied by Nanocomp Technologies Inc.) were mechanically stretched using an AGS-J Shimadzu machine to substantially improve nanotube alignment (see our previous report for more details^[6]). The aligned CNT sheets were placed in *m*-CPBA/dichloromethane solution for epoxidation functionalization, and then washed with dichloromethane to remove residual *m*-CPBA. The functionalized-CNT sheets were placed in a vacuum oven at 80 °C for 30 min to evaporate the residual dichloromethane. Finally, the CNT sheets were impregnated with BMI 5250-4 resin solution to make individual CNT prepreg sheets with approximately 60 wt% nanotube concentration or loading. The prepregging process is a solution impregnation process. The residual solvent (acetone) was removed at 80 °C in the vacuum oven over 2 h to make the BMI/CNT-sheet prepreg. Six prepreg layers were stacked together and cured by a hot-press procedure with high pressure following the

curing cycle: 375 °F for 4 h plus 440 °F for 2 h. The CNT weight fraction in the final composites was about 60 ± 2 wt%.

Characterization: Mechanical property tests were conducted using a Shimadzu machine with crosshead speed of 1 mm min⁻¹ and a gauge length of 20 mm under room-temperature conditions. The strain was recorded by a Shimadzu noncontact video extensometer (DVE-201). The specimens were cut into dog-bone shape with a length of 35 mm and thickness of 60 μm according to ASTM D638. After tensile tests, the fracture surface of the specimens was coated with a gold layer and observed using a scanning electron microscope (JEOL JSM-7401F). DMA was performed on a DMA Q800 machine (TA Instruments Inc.) using the film mode with a constant frequency of 1 Hz from room temperature to 400 °C with a heating rate of 5 °C min⁻¹. The electrical conductivity of the functionalized-CNT-sheet/BMI composites was measured using the four-probe method.

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