

Continuous Carbon Nanotube Reinforced Composites

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ABSTRACT

Carbon nanotubes are considered short fibers, and polymer composites with nanotube fillers are always analogues of random, short fiber composites. The real structural carbon fiber composites, on the other hand, always contain carbon fiber reinforcements where fibers run continuously through the composite matrix. With the recent optimization in aligned nanotube growth, samples of nanotubes in macroscopic lengths have become available, and this allows the creation of composites that are similar to the continuous fiber composites with individual nanotubes running continuously through the composite body. This allows the proper utilization of the extreme high modulus and strength predicted for nanotubes in structural composites. Here, we fabricate such continuous nanotube polymer composites with continuous nanotube reinforcements and report that under compressive loadings, the nanotube composites can generate more than an order of magnitude improvement in the longitudinal modulus (up to 3300%) as well as damping capability (up to 2100%). It is also observed that composites with a random distribution of nanotubes of same length and similar filler fraction provide three times less effective reinforcement in composites.

Structural polymer composites are engineered structures from strong load carrying reinforcements (e.g., carbon or glass fibers) and matrix polymer materials having considerably lower strength and density than the reinforcing phase. The combination of fibers and matrixes often gives rise to high strength materials with minimum weight. Exploitation of nanostructures as filler phase shows promise to advance these composites.^{1,2} After their discovery,³ carbon nanotube reinforced polymer composites have been extensively researched^{1,2,4–11} for their strength and stiffness properties. It is believed that the nanotube could be an ideal reinforcement in composites due to the blend of remarkable properties, including structural, mechanical, electrical, and thermal properties.⁴ However, because of the limited lengths that can be obtained for nanotubes (several hundred micrometers, until recently), studies of continuous carbon nanotube reinforced polymer composites have never been reported. Instead, extensive research^{1,2,4–9} has focused on randomly oriented, discontinuous nanotube composites, which fall into the category of “short fiber composites”.¹² Although short fiber

composites could be interesting for certain applications (e.g., electrically conducting composites), they are not the best for high strength structural composites which require loads to be carried by continuous fibers across the dimensions of the composite structures. Hence, it will be extremely interesting to fabricate composites with continuous nanotubes and test their mechanical properties. In short nanotube composites, the dispersion quality of nanotubes and high viscosity of the composites have been shown to be critical in the manufacturing of nanotube polymer composites. In general, the intrinsic weak van der Waals interactions at the interfaces between nanotube and matrix could result in interfacial slippage.^{2,13–16} As a result, the poor load transfer from the matrix to the nanotubes could be the fundamental limiting factor in attaining very high strength in composites. In order to properly evaluate this scenario, it is paramount that we test continuous nanotube reinforced composite materials.

Recent advances in fabrication of carbon nanotubes allow us to grow them up to several millimeters at length,¹⁷ and this provides an opportunity for fabricating continuous nanotube reinforced composites. It has been reported^{18,19} that free-standing arrays of millimeter long, vertically aligned multiwalled nanotubes exhibit supercompressibility, outstanding fatigue resistance, and viscoelastic characteristics. In this study, we attempt to utilize the free-standing arrays of the nanotubes as continuous reinforcements in polymer

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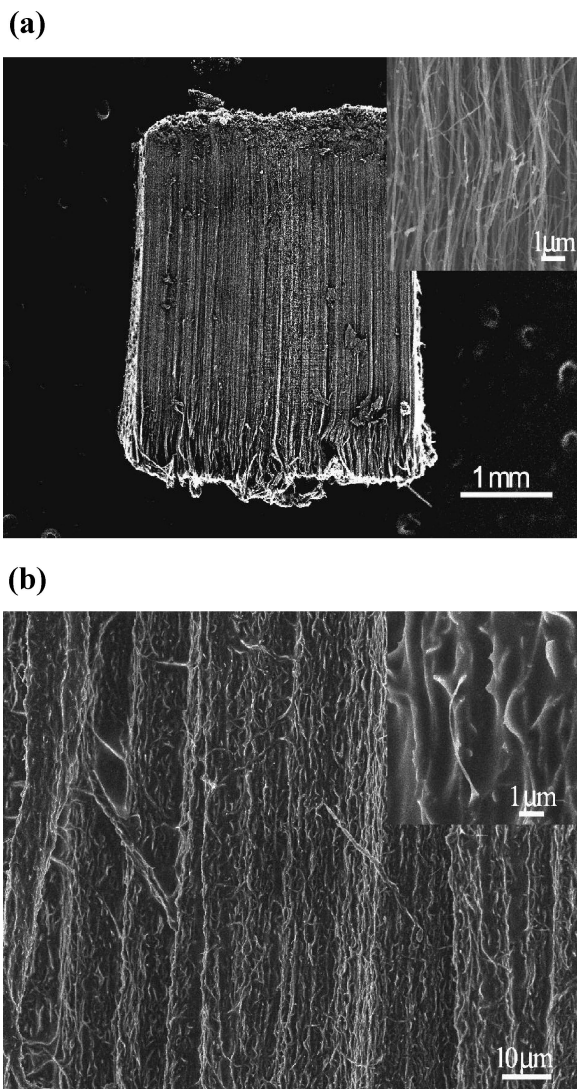


Figure 1. Structural characterization. (a) SEM images of millimeter long vertically carbon nanotube arrays. The excellent vertical alignment of the nanotubes is observed, and high porosity is also seen at a higher magnification (inset), (b) SEM images of continuously reinforced carbon nanotubes–PDMS composite. These images indicate that the PDMS polymer chains are seamlessly infiltrated into open space between nanotubes and that the nanotubes are still maintaining the alignment even after curing process.

composites. Here, we study the compressive mechanical behavior of the continuous nanotubes composites and report that the nanotube composites can generate dramatically enhanced longitudinal (in the direction the nanotubes are aligned) modulus as well as outstanding damping capability under compressive loadings. It is noted that these two properties are typically compromised for most materials. In addition to the mechanical properties, excellent electrical and thermal conductivity of the continuous nanotubes in the composites also add promise for lightweight, multifunctional composites suitable for a variety of engineering applications.

Millimeter-long aligned multiwalled carbon nanotube arrays (Figure 1a) were grown on solid substrates by a xylene-ferrocene CVD process.¹⁷ Ultra long nanotube arrays (~ 3.5 mm high over an area of 2.5×2.5 mm²) were used in this study. The composites were prepared by infiltrating

a polymer into the interstitial spaces of the nanotubes via liquid-state polydimethylsiloxane (PDMS) premixture (Dow SYLGARD 184 silicone elastomer and curing agent, weight ratio of 10:1). The infiltration process was performed in a vacuum chamber at the pressure of 1 Torr for 3 h to not only get rid of air bubbles within the thermosetting polymer (PDMS), but also help the liquid-state monomer seamlessly infiltrate into the empty space within the nanotube arrays. After the monomer infiltration, the composite was left in an oven at 100 °C for postcure. The resultant composites consist of vertically aligned continuous nanotubes as reinforcement and the PDMS as the matrix, in a block shape ($\sim 3.5 \times 2.5 \times 2.5$ mm³). SEM images (Figure 1b) indicate that the intrinsic high porosity (the as-grown nanotube arrays have only around 5% of the volume occupied by nanotubes, rest being empty/air) of the nanotube arrays is completely replaced by the polymer matrix, and the composite can be characterized as a continuous nanotube array composite with about 5% volume fraction of nanotubes (Supporting Information). To investigate mechanical properties of this nanocomposite blocks, mechanical tests were performed with an Instron 5843 testing machine. Compressive axial loading was applied to the composites and compared with pristine (with no polymer infiltrated) nanotube arrays and the pure PDMS polymer, both in the parallel (longitudinal) and in the normal (transverse) direction to the nanotube axis, respectively (Figure 2).

Compressive stress–strain characteristics for three different materials (pure nanotube array, pure polymer, and the composite) with almost identical dimension are compared as shown in Table 1 and Figure 3a–c. The continuous nanotube composite under longitudinal compression (longitudinal composite) exhibits dramatic increase in stiffness over the entire strain range. The composite has the longitudinal modulus of ~ 18.87 MPa between 0 and 8% strain, while pure PDMS shows ~ 2.63 MPa and the nanotube array exhibits ~ 0.55 MPa (Figure 3c). This is a remarkable 600% and 3300% increase in longitudinal modulus compared with the matrix alone and the nanotube array alone, respectively. Compared with the pure nanotube arrays which have plenty of open space occupied by air ($\sim 5\%$ occupancy of nanotubes), the composites need to be subjected to a much higher compressive strain in order to experience local (or shell) buckling under compression.^{20–22} This is because the polymer chains around the nanotubes in the composites strongly influence and make buckling far more difficult. This “confining effect” can, as a result, give rise to the extraordinarily enhanced longitudinal modulus and strength for the nanotube composites by taking full advantage of continuous nanotube reinforcement. Randomly oriented nanotube (the long array nanotubes dispersed in the polymer)–PDMS composites with the same volume fraction (5%) were also fabricated and tested in order to compare with the strength/modulus of the continuous nanotubes composites. Although the randomly distributed nanotube composites have identical volume fraction and same length of nanotubes, Figure 3b indicates that the continuous composite is far more effective in

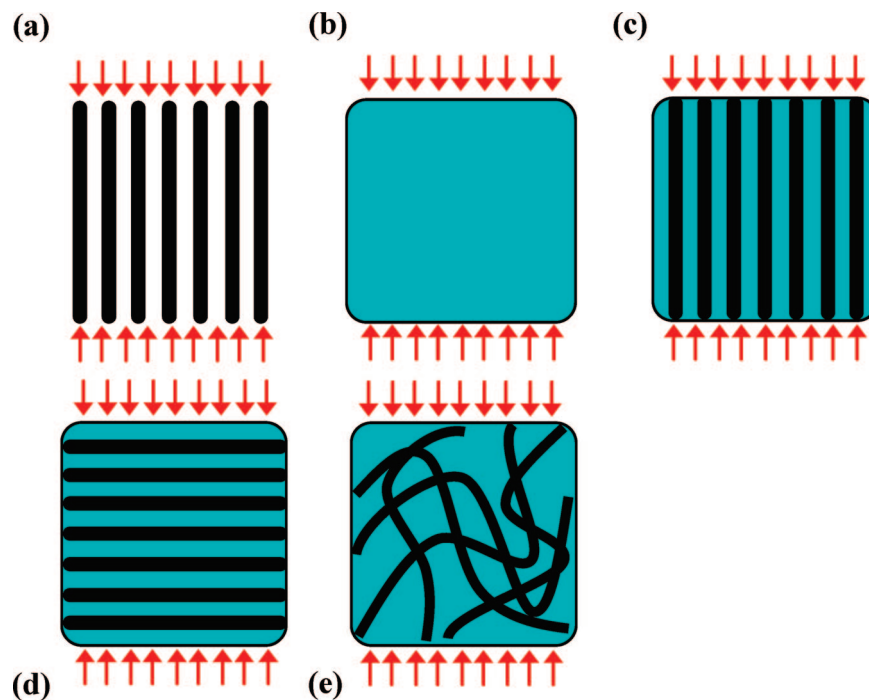


Figure 2. Schematics of different materials tested under compression. (a) Vertically aligned multiwalled carbon nanotube array (with no polymer infiltrated). (b) Pure PDMS matrix (with no nanotube reinforced). (c) Longitudinally loaded continuous carbon nanotubes–PDMS composite (longitudinal composite). (d) Transversely loaded continuous carbon nanotubes–PDMS composite (transverse composite). (e) Randomly dispersed nanotube–PDMS composite (random composite). Note that all of the materials tested in this study have almost identical dimension, which is ~ 2.5 mm in width, ~ 2.5 mm in length, and ~ 3.5 mm in height.

Table 1. Comparison of Compressive Modulus in Monotonic Loads and Dissipated Energy during Compressive Cyclic Loads^a

	continuously reinforced CNT-PDMS Composite	randomly reinforced CNT-PDMS Composite	vertically aligned CNT array	PDMS
longitudinal modulus (MPa) ^b : under compression parallel to the nanotube axis	18.87	6.50	0.55	2.63
transverse modulus (MPa) ^b : under compression normal to the nanotube axis	7.95		1.09	2.63
dissipated energy in longitudinal compressive cycle at strain of 25% (kJ/m ³)	12.16	6.25	1.09	1.48
dissipated energy in transverse compressive cycle at strain of 25% (kJ/m ³)	5.11		0.79	1.48

^a Four different materials, which are the continuous nanotube composite, randomly oriented nanotube composite, pure PDMS, and pure multiwalled carbon nanotube array, are compared for compressive modulus and dissipated energy under both longitudinal and transverse monotonic and cyclic loads, respectively. ^b Note that compressive moduli were measured from the stress–strain response in the strain range of 0–8%.

reinforcement ($> 300\%$ in longitudinal modulus) than random composites.

In addition, the anisotropic properties of the continuous nanotube composites were investigated (Figure 3b). The pure PDMS sample displays identical behavior in both longitudinal and transverse compression, having modulus of around 2.63 MPa between 0 and 8% compressive strain (table 1). We measured a longitudinal modulus of the pure nanotube arrays up to 0.55 MPa (0–8% strain), while a transverse modulus was 1.09 MPa. As previously reported in our earlier work,²³ this difference is attributed to the intrinsic nanotubes' buckling accommodated within the sufficient open space available under longitudinal compression. However, transverse compression mainly leads to elastic densification of the nanotube array.¹⁹ In contrast to the pure PDMS and pure nanotube arrays (which can be considered as nanotube–air composites), interestingly, the nanotube composite, during the longitudinal loading, exhibits unstable stress–strain behavior between 8 and 25% strain (Figure 3b) while during

transverse loading the composite shows no such instability (Figure 3b) in compression over the entire strain range (0–40%), showing response similar to the typical polymers. The instability along the longitudinal direction results from the shell (or local) buckling behavior of the continuous nanotubes, similar to the fiber microbuckling¹² found in carbon fibers; this is considered to be one of the longitudinal compression failure modes. As seen in Figure 3b, in the initial strain region ($\sim 8\%$) the composite in the longitudinal direction shows significant reinforcement effect. However, as strain increases, the nanotubes start buckling, and correspondingly, the composites experience the instability. Here, the nanotubes' waviness or imperfection (Figure 1b) resulting from mismatch shrinkage between the PDMS and the nanotubes during the curing process could result in a range of buckling stress. Whereas the composite loaded along longitudinal direction undergoes the instability in compression, the transverse direction loaded composites show more reinforcement with strain and gradually increase in modulus.

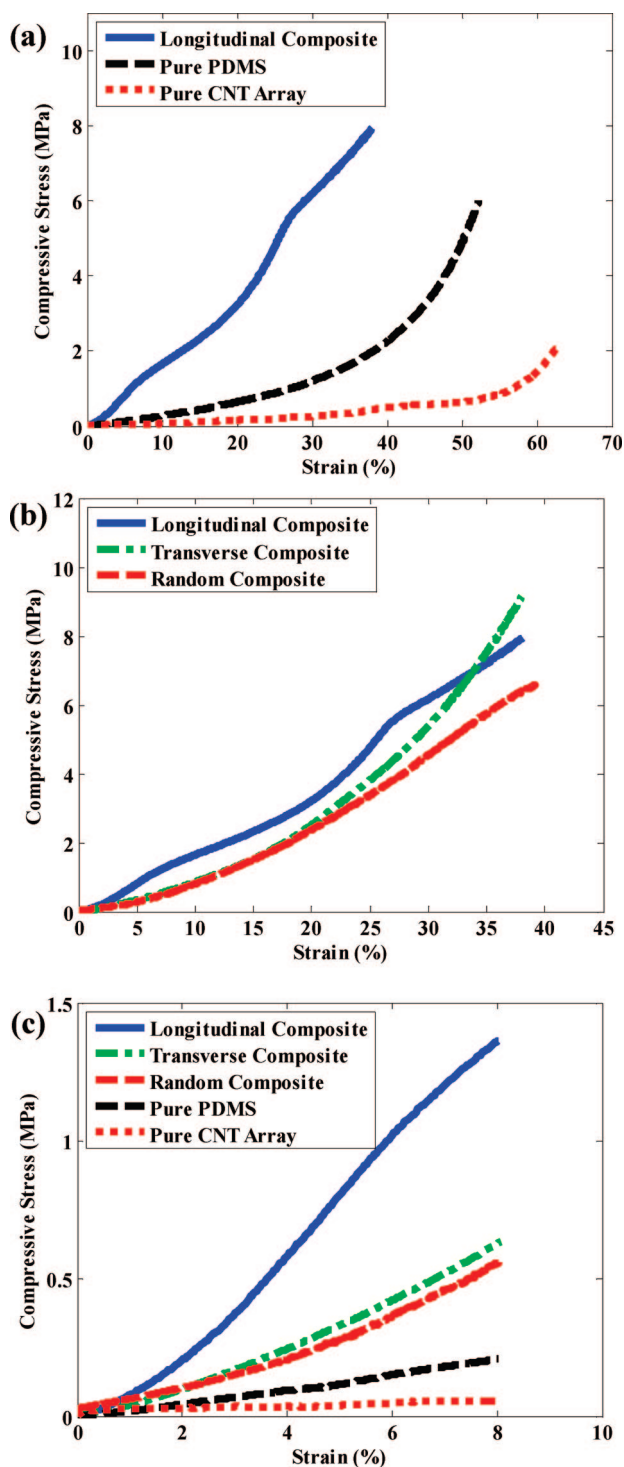


Figure 3. Monotonic compressive stress–strain characterization. (a) Longitudinal composite, pure CNT array, and pure PDMS are compared for their monotonic compressive stress–strain behavior. (b) Anisotropic response in compression is investigated for the continuous nanotube composites, compared with the response of randomly oriented nanotubes composites which have same length and nearly identical volume fraction of nanotubes. (c) All of the composites, pure PDMS, and pure nanotube arrays samples are compared for the compressive stress–strain responses in the low strain region between 0 and 8%.

This is because nanotubes are not buckled in this latter case and instead they come closer to each other under increasing transverse compression; the radial stiffness of nanotubes^{24,25}

now substantially contributes to the observed reinforcement (Figure 3b). Additionally, this explanation is supported by the observation of the compressive stress–strain behavior of randomly oriented nanotube–PDMS composites (Figure 3b). In that case, there is neither the instability nor the sharp increase in modulus as seen in the response of transversely loaded continuous nanotube composites.

We also performed dynamic cyclic tests for all of the materials. Among them, the continuous nanotube composite loaded longitudinally shows the greatest hysteresis loops during the compressive cycles (Figure 4a), indicating substantial mechanical damping. To quantify the damping capability of the composites, we calculated the dissipated energy during compressive cycles at different strain levels between 0 and 25% (Figure 4c). Here, note that the energy dissipated during compression–release is equivalent to the area of the hysteresis loop, which is defined by $\oint \sigma d\varepsilon$, where σ is a measured compressive stress and ε is an applied compressive strain. The composite loaded longitudinally exhibits up to 2100% increase (at 10% strain) in the damping capability compared with the pure PDMS (Figure 4b) and more than 720% (at 25% strain) greater than that of the pure nanotube array. This drastic enhancement of damping property (or hysteresis) can be explained by coupled effect of interfacial sliding^{2,13–16} between nanotubes and PDMS, and thermal conductivity of the continuous composites.²⁶ First, whereas the composite is cyclically compressed at large enough strain, the nanotubes are buckled and then recovered, repeatedly. Interfacial slippage can be promoted, and as a result, frictional energy can be dissipated, since the nanotubes are weakly interacting with the PDMS chains with van der Waals forces. Figure 4c indicates that this composite also exhibits the strongest strain-dissipated energy sensitivity among the composites tested. Particularly, while the cyclic strain is applied at between 8 and 25% strain, where the instability is observed in monotonic compression, the sensitivity sharply increases. In other words, as the strain increases and passes through the unstable region, the frictional energy is rapidly dissipated out of the composites due to the developed local buckling of nanotubes previously discussed. In contrast, the composite loaded transversely has ~95% less energy dissipation (at strain of 25%), since there is not much interfacial slip or local buckling expected. The randomly oriented composite shows slightly greater energy dissipation (22.3% at 25% strain) than the transversely loaded ones during the compressive cycles (Table 1). Second, it is recently reported that unidirectional continuous nanotube composites can have an excellent thermal conductivity along the nanotube alignment,²⁶ implying that the energy dissipation capacity might be better in these composites. This will give a direct impact on hysteresis behavior (or damping) of the composite materials. It is well-known that typically energy can be dissipated in a form of heat (or thermal) in visco-elastic materials. The superposition of the frictional and heat energy dissipation in the nanotube composites loaded longitudinally can result in the observed remarkably enhanced damping capability during compressive cycles.

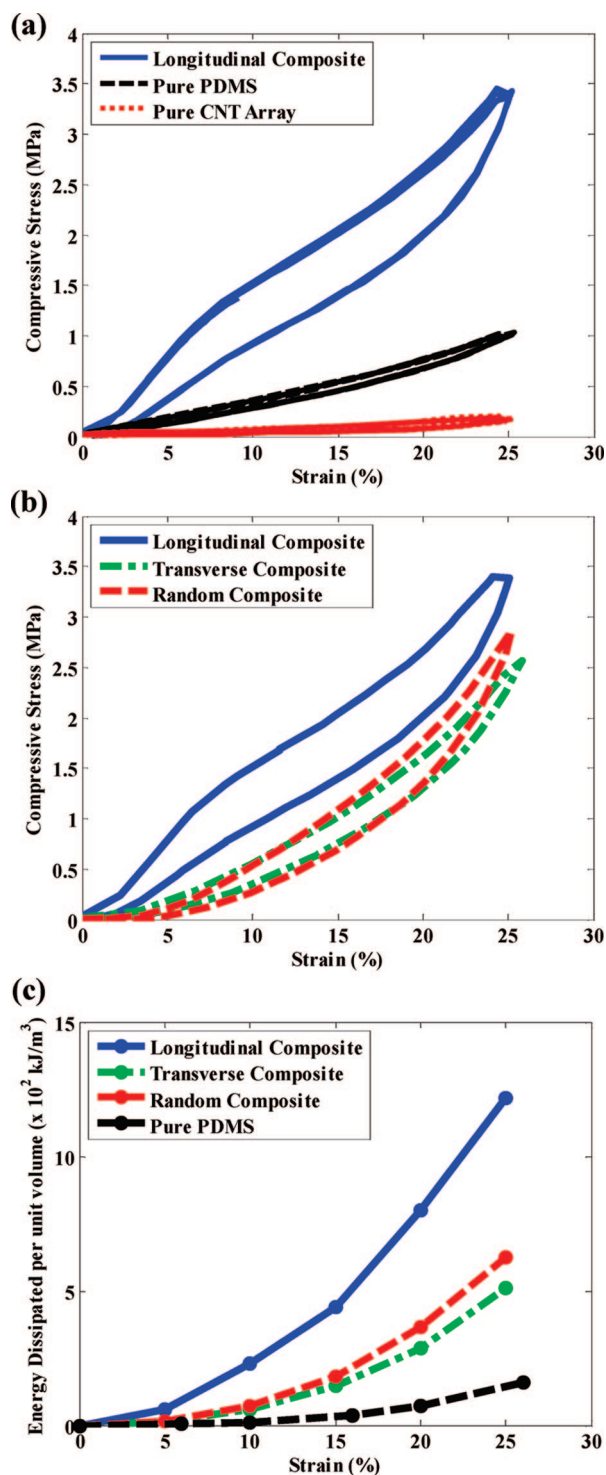


Figure 4. Cyclic compressive stress–strain characterization. (a) Longitudinal composite, pure PDMS, and pure CNT array are compared for the hysteresis behavior under cyclic compression. The longitudinally loaded continuous nanotube composite shows much larger area of the hysteresis loop compared with the pure PDMS and pure CNT array. (b) Hysteresis behavior is investigated for the composite with two different orientation of nanotubes comparing with the behavior of the randomly dispersed nanotube composite (c) Dissipated energy per unit volume is calculated and compared during compressive cycles at different strain levels between 0 and 25%. It can indicate that the longitudinal composite has the greatest damping capability among other materials, and all materials exhibit strain dependent behavior on the damping. Note that all cyclic tests in this study are performed at frequency of 0.5 Hz.

In addition to the mechanical properties under compression, the electrical property of the continuous nanotube composites was characterized. The electrical conductivity of the composite along the nanotube direction was about 4.8 Ohm \cdot cm. The composite also exhibits a strong strain-dependent electrical behavior (Supporting Information Figure 2a). A sensitivity for resistivity of these composites to compressive strains (5~45%) is pretty comparable to that of pure nanotube arrays (Supporting Information Figure 2b).

In summary, continuously aligned nanotube reinforced polymer composites were investigated for the first time. We observed remarkably enhanced compressive modulus/strength, anisotropic characteristics, and damping capability for these materials.

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Supporting Information Available: Density measurements, differential scanning calorimetry results, fabrication process, and electrical conductivity of continuous composites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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