Thermoplastic Elastomer Systems Containing Carbon Nanofibers as Soft Piezoresistive Sensors

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ABSTRACT: Soft, wearable or printable strain sensors derived from conductive polymer nanocomposites (CPNs) are becoming increasingly ubiquitous in personal-care applications. Common elastomers employed in the fabrication of such piezoresistive CPNs frequently rely on chemically cross-linked polydiene or polysiloxane chemistry, thereby generating relatively inexpensive and reliable sensors that become solid waste upon application termination. Moreover, the shape anisotropy of the incorporated conductive nanoparticles can produce interesting electrical effects due to strain-induced spatial rearrangement. In this study, we investigate the morphological, mechanical, electrical, and electro-mechanical properties of CPNs generated from thermoplastic elastomer (TPE) triblock copolymer systems containing vapor-grown carbon nanofiber (CNF). Modulus-tunable TPE gels imbibed with a midblock-selective aliphatic oil exhibit well-behaved properties with increasing CNF content, but generally display nonlinear negative piezoresistance at different strain amplitudes and stretch rates due to nanofiber mobility upon CPN strain-cycling. In contrast, a neat TPE possessing low hard-block content yields a distinctive strain-reversible piezoresistive response, as well as low electrical hysteresis, upon cyclic deformation. Unlike their chemically cross-linked analogs, these physically cross-linked and thus environmentally benign CPNs are fully reprocessable by thermal and/or solvent means.

INTRODUCTION

Concurrent development of portable electronic devices and soft responsive materials is responsible for generating a new class of functional devices for personal healthcare and electronic textiles.1−5 Such devices augment flexible polymeric materials with electronic capabilities for a wide range of sensory applications, such as motion or pulse monitoring.6,7 They can be freestanding as, for example, a wristband8,9 or printed as a thin conductive coating on a substrate, including fabrics.10 While inherently conductive polymers such as polypyrrole are often suitable for these purposes,11–13 they are generally expensive to process and frequently unstable. Conductive polymer nanocomposites (CPNs), consisting of electrically conductive nanoparticles homogeneously dispersed in an elastomeric matrix, constitute viable alternatives to conductive polymers for use in electronic devices.14−21 Important advantages of CPNs for these purposes include the use of nanoscale fillers that can vary in size, shape, species, and therefore conductivity; nanofillers generally possessing a large surface-to-volume ratio that favors surface functionalization to promote dispersability within an organic matrix; facile preparation and application methodologies that are both straightforward and cost-effective; and fabrication that extends from freestanding films exhibiting high extensibility to conformal print layers deposited over large, nonuniform areas. Another attractive aspect of CPNs is that the electrical and mechanical properties are composition-tunable,26 which favors the use of conductive nanofillers possessing a low percolation threshold signaling the onset of a continuous conductive network in the polymer matrix. Excellent examples of nanofillers fulfilling this requirement are carbon black (CB),27 carbon nanotubes (CNTs),28−30 graphene (G),31,32 and carbon nanofibers (CNFs).30,33 Their high surface-to-volume ratio and correspondingly high surface area permit surface functionalization to ensure good dispersion and strong matrix−filler bonding.

In this study, we focus on CPNs containing CNF, which possesses high conductivity levels and relatively low percolation thresholds34 ranging from 0.5 to 2.0 vol %, depending on processing methodology and CNF characteristics.35−37 These nanofillers are particularly appealing because of their facile dispersability in a wide variety of polymer matrices, as well as their lower cost compared to that of CNTs. The elastomers utilized in the present work consist of triblock
copolymers that, with glassy endblocks and a rubbery midblock, behave as thermoplastic elastomers (TPEs). Due to the thermodynamic incompatibility between the chemically dissimilar sequences, these copolymers microphase-separate to form glassy micelles that serve as physical cross-links to stabilize a molecular network composed of bridged midblocks. This elastomer motif extends to TPEs preferentially swollen in a midblock-selective oil, and the phase behavior of, along with the fraction of midblock bridges in, the resulting TPE gels (TPEGs) has been found to depend on copolymer composition, molecular weight, architecture, and concentration. Incorporation of CNFs into the TPEs considered here results in CPNs that can be used as piezoresistive sensors capable of relating sensor resistivity to strain state for real-time monitoring of bodily functions (e.g., respiration and cardiovascular activity) insofar as high-sensitivity sensors possess low strain-cycling hysteresis to maintain superior signal integrity. In one such design, CB-containing TPEs have been reported to exhibit either linear or nonlinear positive piezoresponse wherein resistance increases with increasing strain. While this phenomenon is typically induced in CPNs by in-plane tensile strain, several efforts have likewise demonstrated that strain-reversible piezoresponse in which a negative → positive piezoresponse transition that is repeatable upon strain cycling occurs in CPNs containing anisotropic nanofillers, including G, CNT, and CNF. In the present study, we examine the morphological, mechanical, electrical, and electromechanical properties of CNF/TPE(G) CPNs.

# RESULTS AND DISCUSSION

The present study focuses on the preparation and characterization of soft, low-hysteresis sensory materials that consist of either a neat TPE or an oil-containing TPEG modified with CNF. A representative scanning electron microscopy (SEM) image of the vapor-grown CNFs deposited from suspension is displayed in Figure 1 and qualitatively confirms the nanofiber dimensions listed by the supplier (see the Experimental Section). The enlarged area reveals that some of the nanofibers are at least semiflexible. To ensure a relatively uniform dispersion of CNF in each of the CPNs investigated here, we have concurrently prepared TPE solutions permitted to reach equilibrium and CNF suspensions exposed to high-shear mixing before combining them and subjecting the resultant suspension to additional high-shear mixing. Further heat treatment during melt-pressing assists in both solvent removal and refinement of the TPE morphology. Although we do not provide electron microscopy images or small-angle scattering data of the TPE or TPEG employed in this work, previous morphological investigations have conclusively established that, under the present experimental conditions, both materials exhibit a spherical morphology wherein glassy styrenic (S) micelles are arranged on an unspecified lattice. Due to the size of the midblock relative to each of the endblocks in conventional TPEs (typically with 30−33 wt % endblocks), the most commonly observed morphology consists of “hairy” micelles arranged on a body-centered cubic lattice. In the presence of a midblock-selective oil that can disrupt long-range order, however, face-centered cubic and hexagonal close-packed morphologies have also been reported. While the TPE(G) morphology governs property development, the only morphological aspect of interest here is the presence of spherical micelles, which ensure the highest fraction of midblock bridges needed for a highly elastomeric material.

A series of cross-fracture SEM images acquired at two different magnifications (arranged in rows) from TPEG-based CPNs varying in CNF content from 4 to 6 wt % is provided in Figure 2. In these and subsequent images, the CNF appears bright due to its ability to conduct electrons. At 4 wt % CNF in Figure 2a,d, the nanofibers possess random trajectories and indicate little evidence of long-range correlation. Some large regions observed in Figure 2a appear dark (without CNF), implying that the CNF distribution within these TPEGs is not entirely uniform. As the CNF content is increased to 5 wt % in Figure 2b,e, more nanofibers are visible. Interestingly, regions largely devoid of CNF remain evident in Figure 2b. At the highest CNF fraction examined here (6 wt %), the nanofibers seen in Figure 2c,f are more numerous relative to the earlier images and are more highly correlated. Taken together (Figure 2a–c,d–f), the CNF population and spatial arrangement in these image series can be interpreted to predict that the CPN stiffness (expressed in terms of tensile modulus) and conductivity (expressed in terms of electrical resistivity) both increase with increasing CNF content. These properties are considered further below. Similar morphological trends are apparent in Figure 3 for the TPE-based CPNs at the same CNF loading levels as those in Figure 2. An important difference between the images in Figures 2 and 3 is the absence of relatively large regions that lack CNF in Figure 3. At the lowest CNF fraction (4 wt %) in Figure 3a,d, nanofibers are isolated but uniformly dispersed. In marked contrast, semiflexible CNF seems highly connected at 5 wt % in Figure 3b,e and then highly correlated at 6 wt % in Figure 3c,f. The extent to which the CNF appears correlated in Figures 2c and 3c is qualitatively comparable.

Quasistatic tensile tests of CPNs composed of the CNF-containing TPEG and TPE are presented in Figure 4a,b, respectively, and immediately reveal that the addition of CNF shifts the response curve of each material to progressively higher stresses. This shift is more clearly delineated for the TPEG-based CPNs in Figure 4a due to the inherently lower stresses generated with these soft materials. Since the sensors considered here are not expected to function at very high strain levels, we have not evaluated the ultimate properties of these CPNs at failure (which can exceed 2000% strain for unmodified TPEGs derived from midblock-swollen triblock copolymers). Values of the tensile modulus (E) extracted...
from response curves such as those displayed in Figure 4a,b are included in Figure 4c and indicate that $E$ increases with increasing CNF content in both material systems. While the composition dependence of $E$ is routinely expressed in terms of a mixing rule,$^{23,59−61}$ the increases in $E$ evident in Figure 4c can alternatively be empirically modeled as an exponential function of the form $E = E_0 \exp(\alpha \phi)$, where $E_0$ ideally represents the modulus of the neat TPE(G) without CNF, $\alpha$ is a fitted parameter, and $\phi$ denotes the CNF content (in wt %).$^{a,b}$ Values of $\alpha$ obtained by regression of this expression to

Figure 2. Cross-fracture SEM images acquired from uncoated conductive polymer nanocomposites (CPNs) composed of CNF (bright conductive features) embedded in a styrenic thermoplastic elastomer gel (TPEG, dark nonconductive matrix) at three different loading levels (labeled) and presented at two different magnifications in (a)–(c) and (d)–(f). Each scale bar corresponds to all images in its row.

Figure 3. Cross-fracture SEM images of uncoated CPNs composed of CNF (bright conductive features) embedded in a neat styrenic thermoplastic elastomer (TPE, dark nonconductive matrix) at three different loading levels (labeled) and presented at two different magnifications in (a)–(c) and (d)–(f). Each scale bar corresponds to all images in its row.
the data (with an adjustable $E_0$) are numerically comparable for TPEG- and TPE-based CPNs. Although such similarity between independent $\alpha$ values is comforting, this empirical correlation does not imply a fundamental physical relationship. Rather, the primary purpose of these tensile measurements is to discern the extent to which the mechanical properties of the CPNs change in two related polymer matrices upon addition of CNF. Without mineral oil, the TPE (with $E = 1.28$ MPa) possesses a higher modulus than that of the TPEG (with $E = 0.15$ MPa) by about an order of magnitude, confirming that the addition of a midblock-selective diluent can lower the modulus below that of a neat TPE with a higher rubber content. The ability to tune the properties of TPEGs beyond what is achievable with neat TPEs constitutes an important consideration in the development of soft materials.

Since the current materials are being proposed for sensory applications, their static (i.e., deformation-free) electrical properties must be elucidated as a function of CNF content. For this reason, volume resistivity measurements are provided ranging from about $10^{16}$ to $10^{18}$ $\Omega$ cm. As anticipated from prior studies, incorporation of CNF improves conductivity by reducing the resistivity by several orders of magnitude. In the case of the TPE-based CPNs, the resistivity undergoes a precipitous drop from ca. $3 \times 10^{13}$ to $5 \times 10^6$ $\Omega$ cm, indicative of a percolation threshold between 2 and 3 wt %. In addition to percolation theory (which presumes universal behavior on the basis of network characteristics), a variety of theoretical models interpret the percolation threshold by accounting for such factors as random heterogeneities and quantum tunneling. In marked contrast, the CNF-induced reduction in resistivity for the TPEG-based CPNs does not display an abrupt change in resistivity. Instead, the decrease in resistivity is gradual after remaining almost constant up to 1 wt % CNF. This behavior likely reflects the presence of liquid mineral oil, which wets CNF surfaces and thus hinders contact between neighboring nanoparticles. In addition, volume resistivities measured from both CPN series are observed to converge unexpectedly at 7 wt % CNF. The results presented in Figures 4 and 5 confirm that the addition of CNF to either the TPEG or TPE utilized in this study simultaneously increases both the modulus and conductivity (by reducing the resistivity), which is consistent with the SEM images included in Figures 2 and 3. Morphological dissimilarities, coupled with the nontrivial variation in electrical properties evident in Figure 5, further suggest that the electromechanical properties of TPEG- and TPE-based CPNs can be expected to differ. These properties, critically important for sensor performance, are discussed below.

As described in the Experimental Section, the extent to which the CPNs are uniaxially strained is investigated in conjunction with the elongation, or stretch, rate. Maximum strain values examined here reflect material limitations regarding either signal quality (TPEGs) or matrix integrity (TPEs) upon strain cycling. Cyclic electrical resistance measurements are provided as a function of time (or strain) for TPEG-based CPNs containing 6 wt % CNF and subjected to 10 and 20% strain in Figures 6 and 7, respectively. In each of these figures, panel (a) provides results that are strain-cycled at a stretch rate of 20 mm/min and panel (b) displays analogous...
resistance data collected at 100 mm/min. For comparison, resistance measurements acquired during the first and last full strain cycles for each stretch rate (in mm/min): (a) 20 and (b) 100. In (c), results are displayed as a function of time normalized with respect to the time of a single cycle and correspond to the first and final cycles (solid and dotted lines, respectively) from tests performed at 20 (black) and 100 (red) mm/min. The dashed line (labeled) identifies the normalized time (at 0.5) corresponding to strain reversal.

Figure 6. Cyclic electromechanical measurements presented as a function of time (or, alternatively, cyclic strain) for CPNs composed of TPEG/CNF and exposed to 10% strain at two different stretch rates (in mm/min): (a) 20 and (b) 100. In (c), results are displayed as a function of time normalized with respect to the time of a single cycle and correspond to the first and final cycles (solid and dotted lines, respectively) from tests performed at 20 (black) and 100 (red) mm/min. The dashed line (labeled) identifies the normalized time (at 0.5) corresponding to strain reversal.

piezoresistance during the first and final cycles for both stretch rates. Less consistent results are apparent for the same TPEG-based CPNs subjected to 20% strain in Figure 7. The maximum and minimum resistance values measured at 20 mm/min in Figure 7a are 1.49 ± 0.03 and 0.70 ± 0.07 MΩ, respectively, whereas those corresponding to 100 mm/min in Figure 7b are 1.21 ± 0.05 and 0.53 ± 0.15 MΩ, respectively. In Figure 7c, the more variable results imply inferior piezoresistive behavior, as well as overall signal quality.

The single-cycle data collected at 10% strain and 100 mm/min appear relatively smooth in Figure 6c, but those corresponding to 20 mm/min are significantly noisier. We attribute the resistance fluctuations visible in these data to dynamically occurring changes in CNF connectivity. The nanofibers, residing in an oil-swollen rubber matrix, possess greater mobility than those in oil-free rubber and can change
their position/orientation and thus three-dimensional (3D) connectivity and corresponding electrical conductivity during tensile deformation. In this scenario, the nanofibers generally become more connected as the CPN is uniaxially strained to yield a reduction in electrical resistance (and a corresponding increase in conductance). As time (or strain) increases prior to strain reversal at 10% during each strain cycle in which the CPN is stretched at 20 mm/min, the resistance suddenly, but not completely, reverses due to a loss of CNF connectivity as the nanofibers change their position and/or orientation upon further strain. The abruptness of this change in resistance resembles a rheological slip encountered in filled polymers during shear deformation. As the strain continues, alternating, but often short-lived, fluctuations in resistance continue until the maximum strain (at 10%) is reached. Beyond this point, the CPN is allowed to relax as the load is gradually released and the fluctuations in resistance (which generally increases) remain but are less pronounced and regular. This behavior manifested during the first strain cycle is retained during the last strain cycle, but an increase in crosshead speed to 100 mm/min completely eliminates these fluctuations in Figure 6c. If the strain amplitude is increased to 20% in Figure 7c, the fluctuations become more stochastic and the net reduction in resistance prior to strain reversal appears delayed at 20 mm/min. Even the results acquired at 100 mm/min signify the presence of resistance fluctuations due to nanofiber rearrangement. Thus, although TPEGs exhibit relatively negligible mechanical hysteresis (low irrecoverable strain or set) upon strain cycling incorporated conductive nanofillers retain unexpectedly high mobility, which serves to deteriorate the quality of the electrical signal.

In marked contrast, the piezoresistance results included for the TPE-based CPNs in Figures 8 and 9 verify highly stable signal quality, as well as the existence of strain-induced reversible piezoresistivity. At 20% strain in Figure 8a (20 mm/min) and 8b (100 mm/min), the average values of the measured maximum and minimum resistance are 30.4 ± 0.3 and 12.1 ± 0.3 kΩ, respectively, at 20 mm/min and 39.9 ± 0.3 and 15.2 ± 0.3 kΩ, respectively, at 100 mm/min. These results confirm much less signal variation than that observed at the same strain amplitude for the TPEG in Figure 7a,b. If the strain amplitude is increased to 50% in Figure 9a,b, the extent to which the maximum and minimum resistance values vary clearly increases: 97.8 ± 6.6 and 28.4 ± 0.7 kΩ, respectively, at 20 mm/min and 216 ± 16 and 52.0 ± 4.7 kΩ, respectively, at 100 mm/min. The single-cycle measurements presented in Figure 8c for 20% strain and 9c for 50% strain reveal two important characteristics. The first is that, at 20 mm/min, results from the first and last cycle are nearly indistinguishable, thereby indicating virtually no electrical hysteresis. At 100 mm/min, the resistance at the point of strain reversal decreases noticeably upon strain cycling. This observation provides indirect evidence that either the CNF permanently changes its position upon cycling or the cycling occurs too fast to permit the CNF to return to its original position (and resistance level). The second noteworthy feature is that, in all cases, the resistance initially decreases, exhibits a minimum, and then increases prior to strain reversal. We have previously described such strain-reversible piezoresistivity in terms of three distinct stages of strain-induced changes in CNF percolation due to CNF rotation/straightening and translation along the strain axis.

In stage I, uniaxial strain induces a corresponding reduction in the cross-sectional area of the CPN normal to the strain axis (since the deformation is considered to be isochoric). By doing so, the randomly oriented nanofibers embedded in the polymeric matrix begin to straighten, rotate and align along the strain axis as the glassy micelles formed by the copolymer continue to serve as physical cross-links to stabilize the TPE matrix. During this typically observed electromechanical process, the 3D connectivity of the nanofillers and, consequently, the conductivity of the CPN concurrently increases so that the measured resistance decreases, resulting in negative piezoresistivity. When the strain level reaches a critical value at stage II, however, the extent of CNF connectivity becomes briefly independent of strain. Once the CPN enters stage III, the nanofibers in contact separate due to increased distance along the strain axis, thereby lowering the
overall conductivity of the CPN and promoting positive piezoresistivity. Such strain-reversible piezoresistivity is qualitatively consistent with prior reports, revealing that the maximum conductivity in thermoplastic CPNs containing CNTs occurs at intermediate alignment levels. The unexpected and remarkable aspect of Figures 8c and 9c is that all three stages associated with strain-reversible piezoresistivity are clearly delineated at both of the strain and elongation rate levels examined for the first and final strain cycles.

**CONCLUSIONS**

Soft strain sensors are of growing technological interest in the fabrication of portable healthcare products and wearable electronic devices. In this study, we have examined the morphological, mechanical, electrical, and electromechanical properties of conductive polymer nanocomposites composed of carbon nanofibers embedded in either a neat TPE or an oil-swollen TPEG. Comparison of SEM images acquired from representative specimens confirms that the nanofibers expectedly increase in both population density and local correlation as the nanofiber loading level is increased. As expected, this increase in nanofiber content is accompanied by increases in tensile modulus and electrical conductivity. One distinguishing characteristic differentiates the two nanocomposite series: the one with a TPE matrix exhibits a well-defined percolation threshold, whereas the one with a TPEG matrix does not. This behavior is reflected in profound differences between the electromechanical properties of the two series. Although TPEGs are capable of withstanding continuous strain cycling with relatively little mechanical hysteresis or evidence of fatigue, their generally negative piezoresistive properties display significant fluctuations, especially at high strain amplitudes and low stretch rates, due to strain-induced repositioning and reorientation of the conductive nanofibers, which are less spatially restricted (i.e., mobile) due to the presence of liquid oil. At high stretch rates, the degree of such fluctuations is substantially reduced. In the presence of the neat TPE, however, clearly defined strain-reversible piezoresistivity is manifested at all strain amplitudes and stretch rates. In this case, electrical resistance initially decreases and then switches and increases prior to strain reversal during strain cycling. At low elongation rates, resistance measurements collected from the first and last strain cycles are nearly indistinguishable, thereby indicating that such materials constitute excellent candidates for strain sensors capable of high sensitivity and repeatability.

**EXPERIMENTAL SECTION**

**Materials.** Two poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) triblock copolymers were employed in this work. The first (SEBS1, Taipol 6151) obtained from TSRC/DEXCO was a conventional TPE with 32 wt % S and a number-average molecular weight ($M_n$) of 186 kDa ($D = 1.05$), according to inhouse gel permeation chromatography performed on a Viscotek Max System. The second (SEBS2, Tuftec H1221) with $M_n = 55$ kDa $D = 1.08$) was provided by Asahi KASEI and possessed a much lower S content (12 wt %). An aliphatic white mineral oil with a molecular weight of 567 Da and reagent-grade toluene were purchased from Petroyn Lubricants A.S. and Merck, respectively, and used as-received. Vapor-grown CNF measuring 130 nm on average in diameter and 20–200 μm in length was obtained from Sigma-Aldrich.

**Methods.** The CPN films examined here were produced according to a three-step mixing procedure. In the first step, either the SEBS1 copolymer containing 70 wt % mineral oil or the SEBS2 copolymer without mineral oil was dissolved in toluene for 12 h under agitation at ambient temperature. In the second step, a suspension of CNF in toluene was prepared by adding a predetermined mass of CNF to 10 g of toluene and then subjecting the mixture to high shear in a Kurabo-Mazerustar KK250 planetary mixer for 90 s. In the final mixing step, the polymer solution was added to the suspension and shear-mixed for an additional 90 s. The resultant suspensions were cast into a Petri dish and dried under vacuum for 12 h at 50 °C. Dried films were melt-pressed at 190 °C for 15 min (TPEG) or 180 °C for 3 min (TPE) to a thickness of 0.8–0.9 mm. Specimens from both CPN series selected for examination by SEM were cryofractured in liquid nitrogen prior to mounting. Images of uncoated CNFs and CPNs were...
obtained on a field-emission JEOL JSM-6400 electron microscope (Middle East Technical University) and an ultrahigh-resolution FEI Verios 460L Schottkey emitter electron microscope (North Carolina State University), respectively, both operated at an accelerating voltage of 20 kV. Quasistatic uniaxial tensile strain analysis of the CPNs was performed on a Devotrans DVT universal load frame. For each CPN, three rectangular specimens measuring 25 mm × 5 mm were cut from larger films and tested to determine the nominal (engineering) stress as a function of true tensile strain.

The volume resistivity of each CPN was determined with a Keithley model 6517B electrometer and model 8009 resistivity chamber in accordance with the ASTM D257 standard. Before conducting the electrical measurements, specimen thicknesses were discerned using an Asimeto digital thickness meter. At least five measurements were collected so that average and standard error values could be calculated. To determine the piezoresistive behavior of the CPNs in the longitudinal direction (parallel to the applied strain), specimens measuring 80 mm × 25 mm were attached to four electrical leads spaced 10 mm apart along the centerline of the specimen parallel to the longitudinal direction. The leads were adhered to each CPN surface with a conductive adhesive containing 40 wt % CB prepared for this purpose. Test specimens were clamped on a customized load frame having the gauge length set at 50 mm and subsequently cyclic to 10–50% strain amplitudes at elongation rates of 20 and 100 mm/min to ascertain the effects of strain and stretch rate. Dynamic resistance measurements were simultaneously conducted using a computer-controlled setup consisting of a current source (Keithley 6221) and a nanovoltmeter (Keithley 2182A) under an input current of 1 μA. Resistance was recorded as a function of time, and all CPNs in each series were evaluated for at least 10 continuous loading/unloading cycles at a constant crosshead speed.

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Notes
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■ ADDITIONAL NOTES

“While mixing rules can be written in many different functional forms, the most successful one employed here is a linear rule given by In E_r = (\phi/100) In E_r + (1 - \phi/100) In E_s, where the subscripts c, f, and p refer to the nanocomposite, CNF, and polymer, respectively. We elect not to use this expression, however, since the extracted values of E_r are inconsistent, varying by orders of magnitude, between the TPE and TPEG datasets. We note that the value of E_r discerned from the TPE tensile data (∼93 GPa) is most similar to that reported for CNF in the literature (ranging from about 25 GPa in ref 59 to about 50 GPa in ref 60).

Application of the Cox model described in ref 61 to the two tensile datasets in Figure 4c suggests that the aspect ratio of the CNF in the TPE is significantly smaller (<40) than that in the TPEG (>100). If real, the most likely cause for such a difference is the mechanical mixing employed to disperse the CNF since the TPE possesses a higher melt viscosity.

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