One-step hybridization of graphene nanoribbons with carbon nanotubes and its strong-yet-ductile thermoplastic polyurethane composites

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A hybrid of reduced graphene nanoribbon (GNR)—carbon nanotube (CNT) (i.e. R-GNR/CNT hybrid) with unique three-dimensional (3D) nanostructures has been prepared via a facile unzipping and reducing method. Interlocked structures are formed within the nanohybrids where one-dimensional (1D) CNTs act as bridges connecting individual two-dimensional (2D) GNRs, which not only prevent the aggregation of GNRs but also promote the formation of 3D hybrid with cross-linked nanostructure. Thermoplastic polyurethane (TPU) composites with different R-GNR/CNT hybrid loadings have been fabricated via solution casting. With the addition of small amount of R-GNR/CNT hybrids, apart from the largely improved tensile strength and Young’s modulus, the toughness of the TPU composites is surprisingly enhanced. Here, the toughening mechanisms are also discussed. Furthermore, the electrical conductivities of the TPU composites are also significantly enhanced in the presence of this 3D R-GNR/CNT nanohybrid due to the formation of conductive pathways within the matrix.

1. Introduction

Graphene nanoribbon (GNR), a single atomic layer of sp² carbon atoms with straight edges, could be prepared by chemical vapor deposition (CVD) method [1], spirally or longitudinally unzipping the multi-walled carbon nanotube (MWCNT) [2,3] with unique characteristics including high aspect ratio, low-defect, as well as controllable morphology, which makes it a promising candidate for use in electronic devices, such as field effect transistors [4], and dye-sensitized solar cells [5]. Compared to the commonly used graphene oxide produced by Hummers’ method, the length-to-width ratio and dimension of this GNR produced by splitting carbon nanotube (CNT) can be exactly predetermined by the length and diameter of the initial CNT [6,7]. Although GNR with narrower width less than 10 nm behaves as semiconductor independent of its edge pattern, the wider GNRs exhibit high electrical conductance characteristic of large graphene flakes and could be further used for bulk applications, such as flexible transparent electrodes [7]. Furthermore, the high aspect ratio of wide GNRs makes them particularly attractive of carbon fiber spinning and fabrication of conductive polymer composites [8].

Recently, although hybrid materials of CNTs and graphene (or graphene oxide) have been successfully prepared by solution mixing [9–13] or CVD method [14,15], except for the sophisticated preparation process, the obtained hybrids could hardly ensure a close interaction between CNTs and graphene sheets [16], which seriously limits the further application of the prepared hybrid materials. So, developing a convenient and efficient method for preparing hybrid material of CNTs and graphene (or graphene derivatives, such as graphene) with strong interfacial interaction between these two kinds of carbon materials and realizing their synergistic effect is urgent and of great importance.

In this work, we have facilely prepared a hybrid of oxidized graphene nanoribbon–carbon nanotube (i.e. O-GNR/CNT) by one-step unzipping the MWCNTs. After the pristine MWCNTs have been partially unzipped, unique three-dimensional (3D) cross-linked nanostructures are formed where residual CNTs act as “bridges” connecting the unzipped nanoribbon sheets. Reduced graphene nanoribbon–carbon nanotube (R-GNR/CNT) hybrid is obtained after the O-GNR/CNT hybrid was treated with hydrazine hydrate. With the presence of residual CNTs, not only the aggregation of GNR is prevented, but also the electron transfer efficiency of the hybrid is greatly improved, resulting in an electrical conductivity as high as 120 S cm⁻¹ compared with the 65 S cm⁻¹ of the pristine CNTs. Using this 3D R-GNR/CNT hybrid as nanofililers, a series of thermoplastic polyurethane (TPU) composites were...
fabricated by solution casting method. To our interesting, with the addition of merely 1.0 wt% R-GNR/CNT hybrid, not only the Young’s modulus and ultimate tensile strength of the composite are significantly enhanced, but also the toughness of the composites is greatly improved. Furthermore, due to the excellent dispersion of this 3D R-GNR/CNT hybrid in the TPU matrix, the electrical conductivity of the composites has been enhanced by 9 orders of magnitude with the incorporation of 1.0 wt% R-GNR/CNT hybrid compared with neat TPU matrix.

2. Experimental

2.1. Materials

The pristine CNTs used in this work are MWCNTs, which is produced by chemical vapor deposition method with diameter of 20–30 nm and length larger than 20 μm and purchased from Chengdu Organic Chemicals Co. Ltd. Thermoplastic polyurethane (TPU, Product No. 58277, with a Mn of 100,000 and hard segment content of 44.7%) was used throughout the experiments was supplied by Noveon Inc., USA. Chemical reagents were obtained from Sinopharm Chemical Reagent. Milli-Q ultraclean water was used throughout the experiments. All the materials were directly used in the experiments without further purification.

2.2. Preparation of O-GNR/CNT and R-GNR/CNT hybrids

The O-GNR/CNT hybrid was prepared by the method of unzipping the MWCNTs [17]. The fabrication process can be described as follow: firstly, 100 mg of pristine carbon nanotubes were suspended in 25 mL of concentrated H2SO4 and stirred for 1 h. H3PO4 (85 wt%, 3 mL) was then added and the mixture was allowed to stir for another 20 min at room temperature until the reaction temperature increased to 70 °C. After that, 200 mg of KMnO4 was gradually added into the mixture in 2 h. The reaction was stirred for another 2 h at 70 °C. After being cooled to room temperature naturally, the mixture was poured into 100 mL of ice-water containing 4 mL H2O2 (30 wt%). The mixture was allowed to coagulate for 24 h and the obtained precipitates were dialyzed against ultraclean water for 1 week to remove the residual reagents. After that, a homogeneous dispersion of O-GNR/CNT hybrid was prepared. After being reduced with hydrazine hydrate at 98 °C with stirring for 5 h, a stable dispersion of R-GNR/CNT hybrid in N,N-dimethyl formamide (DMF) was achieved by ultrasonication with sonication power of 250 W for 20 min at room temperature.

2.3. Fabrication of neat TPU, TPU/(R-GNR/CNT) composite films

The TPU/(R-GNR/CNT) composite films were prepared using a typical solution casting method. Typically, 500 mg of TPU pellets were dissolved in 15 mL of DMF at 90 °C. Then, a desired amount of DMF dispersion of R-GNR/CNT hybrid was gradually added into the TPU solution. After being carefully stirred for 30 min followed by sonication for another 30 min, the mixture was subsequently poured into a culture dish. The solvent was slowly evaporated at 70 °C for 24 h to get the TPU/(R-GNR/CNT) composite film with 1.0 wt% nanofiller loading. Similarly, TPU/(R-GNR/CNT) composite films with different hybrid loadings of 0, 0.2, 0.5, 1.5, and 2.0 wt%, respectively, were also prepared.

2.4. Characterization and instruments

X-ray diffraction (XRD) measurements were carried out using a PANalytical X’Pert PRO XRD with Cu Kα radiation (λ = 0.1548 nm; operating energy, 40 keV; cathode current, 40 mA; scan rate, 2° min⁻¹). Fourier transform infrared (FTIR) analysis was performed on a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector by signal-averaging 64 scans at a resolution of 4 cm⁻¹. Raman spectra were collected using an Avalon Instruments Raman Station using a 632.8 nm He–Ne laser. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2100 TEM instrument with an accelerating voltage of 200 kV. The TPU/(R-GNR/CNT) composites for TEM observations were micromoterved under cryogenic conditions to obtain ultrathin sections using a Leica ultramicrotome with a diamond knife. Thermogravimetric analysis (TGA) was performed by using a Perkin Elmer Pyris-1 TGA under nitrogen atmosphere. The tensile tests of the TPU and its composite films were carried out using an Instron universal material testing system at 25 °C with a crosshead speed of 5 mm min⁻¹. Mechanical property values reported here present an average of the results for tests run on at least five specimens. The conductivities of the pristine CNTs and the obtained R-GNR/CNT hybrid were measured using a 4-point probe method (RTS-8) by coating the samples on the glass slides. The electrical conductivities of the TPU composites were measured by a two-probe method using a picoameter (ZC-36, Shanghai Precision & Scientific Instrument Co., Ltd, China), and at least five data points were measured for each sample.

3. Results and discussion

3.1. Characterization and micrographs of pristine CNTs, O-GNR/CNT and R-GNR/CNT

Fig. 1 schematically illustrates the unzipping procedure and the formation process of the unique 3D “ribbon-to-bridge-to-ribbon” nanostructure, where CNTs act as “bridge” connecting different GNR sheets. The pristine CNTs were partially unzipped under treatment of mixed acid and KMnO4, thus forming the O-GNR/CNT hybrid. Under ultrasonication and reduction, the hybridization of the GNR and residual CNTs occurred, resulting in the formation of R-GNR/CNT hybrid with a 3D electrically conductive structure. It is noted that, compared with the amount of KMnO4 used in Ref. [17], here less KMnO4 (2 wt% equal of pristine CNTs) was used in order to
partially unzip the CNTs because the side-walls unzipped from the pristine CNTs were greatly dependent on the amount of oxidizing agent (KMnO₄) [3].

The dispersibility of pristine CNTs, O-GNR/CNT hybrid, R-GNR/CNT hybrid in water, and R-GNR/CNT hybrid in DMF was tested by the sedimentation experiments. The pristine CNTs aggregate and precipitate quickly in water due to strong van der Waals forces among CNTs themselves (Fig. 2a). After the unzipping and purification processes, the obtained brown solid (O-GNR/CNT hybrid) can be easily dispersed in water (Fig. 2b). After that, the chemical reduction of the oxidized R-GNR/CNT hybrid in water was conducted using hydrazine hydrate, and black precipitates were finally formed (Fig. 2c). However, the R-GNR/CNT precipitates can be well dispersed in DMF upon ultrasonication (Fig. 2d).

Fig. 3 shows the XRD analysis of pristine CNTs, O-GNR/CNT and R-GNR/CNT hybrids. The pattern of pristine CNTs exhibits a sharp peak centered at 2θ = 26.0°, corresponding to the interlayer spacing of 3.4 Å. Compared with pristine CNTs, sample O-GNR/CNT hybrid shows two apparent peaks at about 2θ = 10.8° and 2θ = 26.0°, with d-spacings of 8.6 Å and 3.4 Å, corresponding to the existing of oxide nanoribbons and residual CNTs [3]. This result has undoubtedly proven that the pristine CNTs were partially unzipped and hybrid of O-GNR/CNT was successfully formed. Furthermore, after been reduced by hydrazine hydrate, the R-GNR/CNT hybrid has a broad peak at 2θ = 24.8° with a d-spacing of 3.6 Å, a value close to the interlayer spacing of graphite (3.5 Å) [18], suggesting the removing of residual oxygenated groups and recovery of π-conjugated structure from O-GNR/CNT hybrid upon chemical reduction.

TEM images have actually and vividly confirmed the successful unzipping of the pristine CNTs and the formation of 3D hybrids of O-GNR/CNT and R-GNR/CNT (as seen in Fig. 4). Compared with pristine CNTs (Fig. 4a), large number of GNRs homogeneously co-dispersed with the residual CNTs can be clearly found in the O-GNR/CNT hybrid (Fig. 4b), forming a unique hierarchical structure, and further confirming the results of XRD analysis. Fig. 4c and d shows the TEM images of the R-GNR/CNT hybrid at low and high magnifications, which further provide evidence of co-existence or hybridization of GNRs and CNTs.

The residual CNTs adsorbed on different GNRs not only prevent the aggregation of GNRs but also play a role of “bridges” to form a unique “ribbon-to-bridge-to-ribbon” nanostructure, resulting in an improved electrical conductivity of 120 S cm⁻¹ compared with the 65 S cm⁻¹ of the pristine CNTs. It is worth to mention that, the interfacial interaction between GNR and CNT is so strong that they cannot be completely separated even under high centrifugation at 8 × 10⁴ rpm. These features could be the main reasons for the largely improved mechanical and electrical properties of the polymer composites incorporated with this new type of fillers, which will be discussed below.

Raman spectroscopy is used to further evaluate the structure of samples we have prepared, as seen in Fig. 5. Pristine CNTs (Fig. 5a) display bands at 1342 and 1575 cm⁻¹, corresponding to the well-documented D and G bands, respectively. However, in agreement with previous reports for chemically reduced graphene oxide [19], the D bands of both of the O-GNR/CNT (Fig. 5b) and the R-GNR/CNT hybrids (Fig. 5c) at 1350 cm⁻¹ were enhanced and broadened, compared to the starting pristine CNTs. This data means the increase of lattice distortions and structural defects, indicating that some side-walls of pristine CNTs were successfully opened [20]. The unexpected increase of I_D/I_G ratio from 1.0 for the O-GNR/CNT hybrid to 1.4 for the R-GNR/CNT hybrid could be explained that reduction increases the number of small domains of aromatic structure responsible for the D band, but not necessarily for their overall size, which is responsible for the G band [17].

The successful reduction of sample O-GNR/CNT hybrid was further confirmed by FTIR spectra and TGA analysis. Fig. 6 shows the FTIR spectra of pristine CNTs, O-GNR/CNT and R-GNR/CNT. The pristine CNTs (Fig. 6a) have weak absorption peaks centered at 1040 and 1582 cm⁻¹, corresponding to the existence of C–OH and C=C groups, respectively. However, for the O-GNR/CNT hybrid (Fig. 6b), new absorption peaks appear at 1720 and 1228 cm⁻¹ emerged, which corresponds to the C=O and C–O–C stretching, respectively. The appearance of the characteristic peaks at 1040 and 3410 cm⁻¹ indicates that a large number of –OH groups have been introduced to the surfaces of GNRs and CNTs, which further confirms that the pristine CNTs have been successfully unzipped [3,20]. For the R-GNR/CNT hybrid (Fig. 6c), the C=O vibration band at 1720 cm⁻¹ disappears and the intensities of O–H and the C–O stretching bonds diminish, which means the removal of most of the oxygen-containing groups. Meanwhile, as the result of the restoration of sp² structures during the reduction process, the absorption band at 1582 cm⁻¹ corresponding to C=C groups can be observed clearly (Fig. 6c). Fig. S1 shows the TGA results of the samples. The O-GNR/CNT hybrid shows a significant weight loss from 180 to 270 °C, which corresponds to the cleavage of large amount of oxygen-containing functional groups, such as carbonyl and carboxyl groups [21]. In contrast, the R-GNR/CNT hybrid does not show
apparent weight loss stage, indicating that most oxygen-containing functional groups have been removed from the surface of GNRs and CNTs during the chemical reduction [22]. Therefore, these results undoubtedly indicate a successful reduction of the O-GNR/CNT hybrid to the R-GNR/CNT hybrid, which results in the formation of 3D hybrid material with electrically conductive network.

3.2. Mechanical properties of TPU composites

The stable and uniform dispersion of R-GNR/CNT hybrid in DMF makes it possible for fabricating TPU-based composites using the conventional solution casting method. Here, the dispersion state of R-GNR/CNT hybrid in TPU matrix was investigated. TEM images of ultrathin section of TPU/(1.0 wt% R-GNR/CNT) composite taken at different magnifications are shown in Fig. S2. The dark areas are R-GNR/CNT hybrid, and the gray regions represent the TPU matrix. It can be seen that the R-GNR/CNT hybrid was homogeneously dispersed at nanoscale levels throughout the matrix without the formation of large aggregates. When further increasing the R-GNR/CNT loading level (such as 2.0 wt%), however, the aggregation of R-GNR/CNT is observed (Fig. S3).

The typical stress–strain curves of the TPU composites with different R-GNR/CNT hybrid loadings are shown in Fig. 7 and the

![Fig. 4. TEM images of (a) pristine CNTs, (b) O-GNR/CNT hybrid, and R-GNR/CNT hybrid at (c) low and (d) high magnifications.](image)

![Fig. 5. Raman spectra (excitation at 632.8 nm) of (a) pristine CNTs, (b) O-GNR/CNT hybrid, and (c) R-GNR/CNT hybrid.](image)

![Fig. 6. FTIR spectra of (a) pristine CNTs, (b) O-GNR/CNT hybrid and (c) R-GNR/CNT hybrid.](image)
mechanical property data are further summarized in Table 1. It can be seen that with the incorporation of only 1.0 wt% R-GNR/CNT hybrid, the tensile strength (31.3 MPa) and the Young’s modulus (32.9 MPa) of the neat TPU are substantially improved by about 184% (88.0 MPa) and 81% (59.7 MPa), respectively (Fig. 8). These largely improved Young’s modulus and tensile strength can be attributed to the fine dispersion of R-GNR/CNT hybrid throughout the TPU matrix along with good interfacial interactions between the hybrid fillers and polymer matrix [23–28]. The toughness is determined by dividing the area under stress–strain curves with the density of the materials, which is found to have been improved from 68 J/g for neat TPU to 247 J/g for TPU/(1.0 wt% R-GNR/CNT) composite (Fig. 9), indicating that an enhancement of 260% has been achieved. Such an unexpected remarkable enhancement in toughening behavior may be closely related to the unique structure of the assembled 3D R-GNR/CNT hybrid which will be discussed later. When the content of R-GNR/CNT hybrid is higher than 1.0 wt %, the Young’s modulus, tensile strength and elongation at break of the composites decrease gradually, which may be ascribed to partial or slight aggregation of the R-GNR/CNT hybrid at higher loading levels. Once the filler aggregation is formed in the composites, it will act as the stress concentration site, thus resulting in a weakening effect for the reinforcement of composite materials [29].

3.3. Toughening mechanism

Hybrid nanofillers for enhancing the mechanical properties depend on their intrinsic features, such as the interwall sliding within CNTs [30], CNT/matrix interfacial adhesion and sliding [31]. Here, the strengthening and toughening mechanisms may be mainly explained with the crosslinking methodology [32]. It has already been proven theoretically that cross-linked structure can significantly improve the overall composite strength and toughness [33–39]. In this work, our observation suggests that the toughening mechanism for the TPU composites originates from synergistic and multiple actions of cross-linked structure, stretching or reorganization of curly CNTs and GNRs, as well as interface sliding between CNTs and GNRs. Firstly, for the strong interfacial interaction between the carbon nanofillers and TPU, the majority of TPU soft segments are likely to be bounded on the surfaces of GNRs and CNTs [40], which will form the cross-linked structure (Fig. S4a) and play an important role in improving the toughness. For example, due to the strong interaction between the functionalized graphene and soft segments of PU, the elongation at break of the composites loaded with only 2 wt% graphene nanosheets has been increased to 386%, compared to 195% for the neat PU matrix [41]. Therefore, thus a cross-linked structure formed from interfacial interaction in our studied system may make a significant contribution to enhance the material toughness (i.e. from 68 kJ/g for neat TPU to 247 kJ/g for TPU composite with 1.0 wt% R-GNR/CNT hybrid). Secondly, just as the tube-like CNTs dispersed in polymer matrix which can be deformed during the stretching process [42], the graphene nanosheets can also form “hill” and “valley” morphology when aromatic molecules are adsorbed at different sites on their surface [43], which inevitably results in the formation of substantial corrugation or curly morphology. In this work, the corrugated or curly GNRs and CNTs within the matrix can be stretched or realigned upon

Table 1
Summary of mechanical properties of neat TPU and its composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
<td>32.9 ± 1.8</td>
<td>31.3 ± 5.3</td>
<td>545 ± 18.4</td>
</tr>
<tr>
<td>TPU/(R-GNR/CNT) (0.2 wt%)</td>
<td>35.0 ± 2.2</td>
<td>54.4 ± 7.0</td>
<td>795 ± 45.1</td>
</tr>
<tr>
<td>TPU/(R-GNR/CNT) (0.5 wt%)</td>
<td>46.6 ± 2.9</td>
<td>64.3 ± 5.8</td>
<td>750 ± 42.3</td>
</tr>
<tr>
<td>TPU/(R-GNR/CNT) (1.0 wt%)</td>
<td>59.7 ± 4.9</td>
<td>88.9 ± 5.4</td>
<td>744 ± 41.2</td>
</tr>
<tr>
<td>TPU/(R-GNR/CNT) (1.5 wt%)</td>
<td>37.2 ± 2.4</td>
<td>54.5 ± 6.2</td>
<td>676 ± 34.6</td>
</tr>
<tr>
<td>TPU/(R-GNR/CNT) (2.0 wt%)</td>
<td>40.1 ± 3.4</td>
<td>36.1 ± 4.6</td>
<td>615 ± 22.0</td>
</tr>
</tbody>
</table>
deformation (Fig. S4b). As a result, the elongation or extension of the curly GNRs and CNTs may play a primary role for absorbing or dissipating the fracture energy during the deformation process. Thirdly, since the interface sliding usually acts as another principal role for transferring the load and given that the π-π interaction within the R-GNR/CNT hybrid could not be ignored, it has been experimentally confirmed by single molecular force spectroscopy that the interaction energy between pyrene rings and graphene surface is as high as 26 kJ mol\(^{-1}\) [44]. Thus the CNTs adsorbed on the surface of GNRs will need a considerable amount of energy to dissociate from the GNRs for having more aromatic structure [45]. So the interface sliding between the GNRs and the CNTs happened during the tensile stretching (Fig. S4c) will also contribute to the toughness improvement to a certain degree. Considering from another aspect, compared with the case for improving the toughness of TPU (from 95 MPa m\(^{1/2}\) for neat TPU to 140 MPa m\(^{1/2}\) for TPU composites with 2 wt% functionalized graphene loading) with the effect of intermolecular interaction and interface sliding simultaneously [46], it is clear that the remarkably improved toughness with 260% enhancement in our work comes from a highly efficient synergistic effect of several factors at least including intermolecular interaction, interfacial sliding and tropism of coiled GNRs and CNTs.

The interfacial interaction between R-GNR/CNT hybrid and TPU matrix has been investigated by FTIR spectra, as shown in Fig. S5. For the TPU composite (curve b), together with the absorption band of carbonyl at 1726 cm\(^{-1}\), the stretching and bending vibrations of the N-H groups occurred at 3310 cm\(^{-1}\) and 1528 cm\(^{-1}\) are indicative of the presence of urethane moieties [41]. Also, it can be clearly seen that the band at 3452 cm\(^{-1}\) for hydroxyl groups in the R-GNR/CNT hybrid disappears in the FTIR spectra of TPU composite, confirming the formation of covalent bonding between the R-GNR/CNT hybrid and TPU chains [47,48]. It should be mentioned that, as the R-GNR/CNT hybrid (curve c) shows no obvious absorption in the infrared range, there is no apparent change in the FTIR spectra of TPU composite compared with the spectra of neat TPU after incorporating the R-GNR/CNT hybrid.

### 3.4. Electrical conductivity and thermal stability of the composites

Graphene and CNTs have also been intensively investigated as conductive nanofillers for enhancing the electrical performance of the polymer matrix due to their intrinsic conductivity [49–51]. Fig. 10 shows the electrical conductivity of the TPU composites versus R-GNR/CNT hybrid contents. It can be seen that with the addition of only 0.2 wt% R-GNR/CNT hybrid, the electrical conductivity of the composite was increased to 10\(^{-5}\) S cm\(^{-1}\), dramatically higher than 10\(^{-11}\) S cm\(^{-1}\) for neat TPU. For the composite with R-GNR/CNT hybrid loading level of 2.0 wt%, the electrical conductivity reached 1.3 × 10\(^{-2}\) S cm\(^{-1}\). The dramatic enhancement of the electrical conductivity of the composites with such low R-GNR/CNT hybrid contents can be attributed to the homogeneous dispersion of 3D nanostructured R-GNR/CNT hybrid in TPU matrix and the formation of effective conductive pathways composed of R-GNR/CNT hybrid within the matrix.

Fig. 11 shows the thermal stability of neat TPU and its composites with different loadings of R-GNR/CNT hybrid. The thermal decomposition temperature (at 10% weight loss) was increased from 325 °C for neat TPU to 338 °C for the TPU composite with 1.5 wt% R-GNR/CNT hybrid. The enhanced thermal stability of TPU composites with low loading levels of R-GNR/CNT hybrid may be attributed to a combined effect of the excellent thermal stability of R-GNR/CNT hybrid as well as the presence of strong interfacial interaction between the TPU matrix and the hybrid nanofillers, especially the interlocked nanostructures formed within TPU matrix.

### 4. Conclusions

In this work, O-GNR/CNT hybrid has been facilely prepared by a one-step unzipping method. After been reduced, the R-GNR/CNT hybrid with a unique 3D hierarchical structure has been successfully prepared. By acting as “bridges” between different GNR sheets, the residual CNTs not only prevent the aggregation of GNRs but also promote the formation of a novel 3D cross-linked or interlocked nanostructure as an electrically conductive network, resulting in an improved electrical conductivity of 120 S cm\(^{-1}\) compared with the 65 S cm\(^{-1}\) of the pristine CNTs. Using this novel R-GNR/CNT hybrid as the nanofiller, a series of TPU composites showing excellent mechanical properties have been fabricated. Compared to neat TPU, the composites possess significantly enhanced tensile strength, toughness, and electrical conductivity. The toughening and strengthening mechanisms of this kind of polymer composites have been discussed. During the tensile deformation process, different factors (e.g. interaction between hybrid and polymer matrix, tropism of coiled GNRs and CNTs, interfacial sliding) play important roles in load transfer and energy dissipation.
Furthermore, this work provides a way for fabricating hybrid nanomaterials and further enlarging their application scope.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.04.013.

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