PET/Graphene Compatibilization for Different Aspect Ratio Graphenes via Trimellitic Anhydride Functionalization

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ABSTRACT: Two trimellitic anhydride-functionalized, thermally reduced graphenes with different aspect ratios, A\textsubscript{f} and the same C/O ratio (8:1) were prepared and melt-mixed into poly(ethylene terephthalate) (PET), and the mechanical properties of the resulting nanocomposites were studied with a focus on plastic deformation behavior. A slight increase in the G' of the melt was observed for the surface-modified low-A\textsubscript{f} graphene composites (A\textsubscript{f} = 20) below the percolation threshold, whereas a significant enhancement in G' was observed for higher-A\textsubscript{f} graphene composites (A\textsubscript{f} = 80) at all graphene loadings, both below and above the percolation concentration. Furthermore, the use of modified low-A\textsubscript{f} graphene caused an improvement both in Young’s modulus and elongation at break of the resulting PET nanocomposites because of enhancement of interfacial adhesion between filler and matrix which resulted in the formation of a coupled network via covalent bonding and the suppression both of strain-induced orientation and strain-induced crystallization. By contrast, the use of modified higher-A\textsubscript{f} surface graphene in nanocomposites caused a drastic improvement in Young’s modulus but lower elongation-at-break than with the unmodified counterpart; the former effect is due to the formation of denser coupled networks and stronger interfacial adhesion as a result of graphene surface modification and the latter is due to the added geometrical restriction in entanglement chains from the PET matrix in the presence of higher-A\textsubscript{f} graphene. The preceding observations demonstrate the potential impacts of tuning both surface chemistry and aspect ratio of graphene in the fabrication of PET/graphene composites.

INTRODUCTION

The fabrication of polymer nanocomposites via the inclusion of nanoparticles into the polymeric matrix has become a standard practice to improve the properties of the resulting composites compared with those of the parent polymers. Two-dimensional (2D) disc-shaped nanoparticles perform better than spherical nanoparticles in terms of improving mechanical properties, gas-barrier properties, and dimensional stability of the resulting nanocomposites.\textsuperscript{1,2} Modified clay\textsuperscript{3,4} and graphene\textsuperscript{5,6} are commonly relied on disc-shaped nanofillers. Graphene has attracted considerable attention on account of its large modulus (250–1000 GPa\textsuperscript{5}), high electrical conductivity,\textsuperscript{6} and high thermal conductivity.\textsuperscript{7}

Poly(ethylene terephthalate) (PET) is a high-performing semicrystalline thermoplastic with elevated glass transition temperature (T\textsubscript{g}), mechanical properties, chemical resistance, and moldability, making it a good candidate for commercial usage in bottles, cartridge, textile fibers, and films.\textsuperscript{8,9} The processing for PET pellets typically involves extrusion as sheets, after which tentering, post-T\textsubscript{g} annealing, and other processing techniques are carried out.\textsuperscript{10–14} Finally, depending on the application of interest, the processed polymer may be postprocessed into the desired shape via automated techniques such as cutting, coating, laminating, and molding.

The property enhancement of PET/graphene nanocomposites compared to that of pristine PET has already been reported elsewhere in the literature.\textsuperscript{21–25,34,42–46} For instance, it has been demonstrated that (1) graphene is more effective than graphite at improving the electrical conductivity of PET composites,\textsuperscript{21} (2) in situ polymerization yields composites of higher conductivity than melt-blending,\textsuperscript{25} and (3) graphene inclusion causes enhancement in the mechanical properties,\textsuperscript{23,24,43} gas-barrier properties,\textsuperscript{42,44} and thermal conductivity of PET.\textsuperscript{34} These advantages of PET/graphene nanocomposites mean that it has the potential for usage in various applications, including, but not limited to, molded structural parts, textiles, cartrdiges, and films with antistatic, electromagnetic-shielding, gas-barrier, and/or heat-dissipation properties. These materials find usage in clothing, vehicles, electrical devices, and packaging materials. The drawback of classical PET/graphene nanocomposite fabrication techniques is that usually one or more of the mechanical properties (flexibility and elongation at...
break) are compromised as more graphene is loaded into the nanocomposite samples. This severely limits the potential of PET/graphene composites for commercial usage because of concerns over industrial-scale fabrication and quality assurance. Shim et al.\textsuperscript{45} were able to overcome the aforementioned issue by chemically functionalizing graphene oxide (GO) prior to preparing the PET-based nanocomposites, a compatibilization step which helped ensure that all the major mechanical properties were enhanced in the resulting nanocomposites (including elongation at break). The problem with this approach is its reliance on solution-processing rather than melt-blending for the fabrication of the composites to avoid elevated temperatures which could end up thermally reducing GO.\textsuperscript{47} The simplicity of melt-processing makes it desirable in the industry as a fabrication method for such composites, so it is useful to modify graphene while still using melt-blending to prepare the nanocomposites.

Our previous study addressed this problem, reporting on the functionalization of graphene with trimellitic anhydride groups and its effect on melt-mixing graphene with PET in composites.\textsuperscript{46} This functionalized graphene, Modi-G1, dispersed in PET without a noticeable change in dispersion levels compared to unmodified graphene, G1, but still succeeded at creating a physically cross-linked system between the polymer and graphene filler during the blending stage, producing melt-mixed PET/graphene nanocomposites which were less brittle than their unmodified graphene counterparts because of a combination of stronger interface adhesion and the restriction of chain mobility which occurs during deformation as a result of strain-induced orientation and strain-induced crystallization.\textsuperscript{46}

The purpose of the current work is to expand trimellitic anhydride functionalization to graphenes with different aspect ratios and to study the difference in effects of said functionalization on the properties of the resulting melt-mixed PET/graphene nanocomposites. In this work, we selected two graphenes of different aspect ratios, $A_p$, and surface-functionalized each with trimellitic anhydride. The modified graphenes were then melt-mixed into PET, and the internal structure (dispersion level and interface) of the resulting PET/graphene nanocomposites was investigated using transmission electron microscopy (TEM) and by measuring their electrical resistance and melt rheology.

\section*{RESULTS AND DISCUSSION}

\textbf{Surface Modification of Graphene.} The typically low C/O ratio of graphene confers a hydrophobicity which results in poor adhesion with polyester.\textsuperscript{48} For this reason, functionaliza-
tion of graphene was first conducted to enhance the interfacial adhesion between the polymer and filler, as depicted in Scheme 1, and demonstrated in a prior work.46 Graphene produced via chemical/thermal reduction of GO typically contains a variety of oxygen-containing groups including C=O, C−OH, C−O−C, COOR, anhydride, lactone, COOH, and chemisorbed water and oxygen.49−53 The most chemically reactive of these surface groups for functionalization are the carboxylic acid, hydroxyl, and epoxy group; the former two in particular can be reacted with by acid chlorides.54,55 For this reason, an acid chloride carrying the trimellitic anhydride was used to functionalize the graphene surface groups (in the presence of pyridine to catalyze the reaction), the acid chloride reacting with the surface and leaving behind a surface-tethered trimellitic anhydride group.

Figure S1 demonstrates the Fourier-transform infrared (FT-IR) spectra for graphene before and after functionalization. Because graphene contains a lower percent of chemically bonded oxygen, some specific peaks are hidden by the strong absorption of the graphite structure and carbonyl groups of graphene.56 In particular, TRG2 and Modi-TRG2 showed stronger absorption than G1 and Modi-G1, rendering it difficult to completely remove the background for the former spectra and making it necessary to greatly enlarge the spectra to find specific peaks, as a result of which the spectra of TRG2 and Modi-TRG2 are far less-resolved than those of G1 and Modi-G1. In spite of the abovementioned measurement challenges, both the modified graphenes demonstrated aromatic C−C stretching peaks in the benzenoid region (wavenumber around 1470 cm⁻¹ as shown in Figure S1).57−59 Moreover, the absorption at 1200 cm⁻¹ was assigned to C−OH while the one at 1580 cm⁻¹ was assigned to aromatic (quinoïd) C=C stretching.57 It is noted that the ratio of C−OH to C=C peak intensity drops post-treatment with acid chloride, indicating esterification of the surface OH groups.46

X-ray photoelectron spectroscopy (XPS) was performed on the samples to identify and quantify functional groups, as done in our previous studies.46 Both survey and high-resolution scans of C 1s and O 1s for the graphenes (unfunctionalized/functionalized) are depicted in Figures 1, S2, and 2. The peak integrations for the O1s peak are summarized in Table 1.

Table 1. Results of the Fitting of the O 1s Region, Values Given in % of Total Intensity

| binding energy (eV) | C=O | C−OH | C−O−C | COOR, anhydride lactone | COOH | chemical absorbed H₂O or O₂ |
|---------------------|-----|------|-------|---------------------|------|-----------------------------|
| G1                  | 17.6| 48.1 | 22.3  | 9.1                 | 2.7  |                             |
| Modi-G1             | 18.3| 14.7 | 49.3  | 11.2                | 6.4  |                             |
| TRG2                | 17.4| 47.8 | 24.9  | 7.4                 | 2.4  |                             |
| Modi-TRG2           | 19.8| 14.5 | 48    | 8.1                 | 9.6  |                             |

All graphenes are observed to consist only of carbon and oxygen (Figure 1), with survey scans showing no observable peaks of N 1s and Cl 2s in G1, Modi-G1, TRG-2, and Modi-TRG2 as a result of using pyridine/N,N-dimethyl formamide (DMF) and acid chloride, respectively. Additionally, the C/O ratio of all four graphenes is measured to be 8:1. Moreover, the unfunctionalized and functionalized graphenes both show similar high-resolution scans for the C 1s peak (Figure S2), while high-resolution scans of O 1s show some difference in peaks between the two sets of materials (Figure 2). Deconvolution of the O 1s peak revealed five bonding environments: C=O (531.1 eV); C−OH, C−O−C (532.3 eV); COOR, anhydride, and lactone (533.3 eV); COOH (534.2 eV); and chemisorbed water and oxygen (536.1 eV).49−51 The most frequently occurring bonding environment in any unmodified graphene is the (C−OH, C−O−C) environment, as demonstrated by the prominent peak at 532.3 eV for G1 and TRG2 (Figure 2a). Surface functionalization results in most of the C−OH groups reacting with their acid chloride groups by alkoxy dehalogenation as demonstrated in our former work,46 forming COOR grafting sites for the trimellitic anhydride groups on the graphene surface, as indicated by the sharp increase in intensity of the COOR, anhydride, and lactone peak (Figure 2c,d and Table 1) in
Modi-G1 and Modi-TRG2. Moreover, it may be noted that the distribution of O 1s bonding environments is quantitatively similar in G1 and TRG2, with G1 containing slightly more alcohol and carboxyl groups, and chemisorbed (hydrogen-bonded) water, while TRG2 contains more lactone groups. Finally, Modi-G1 and Modi-TRG2 are also similar in terms of O 1s bonding environments. Because the C/O ratio is the same in G1 and TRG2 with similar functional group surface distribution, this leads to the modified graphenes also having the same C/O ratio and surface group distribution. In other words, G1 and TRG2 can be compared head-to-head in terms of the aspect ratio while safely assuming them to have the same C/O ratio and chemical surface functionality and the same can be argued for Modi-G1 versus Modi-TRG2. This simplifies the analysis because it means there is one parameter to compare the two graphene systems: aspect ratio.

Figure 3 depicts the TGA thermograms of the unfunctionalized and functionalized graphenes. First, the weight of unmodified graphene decreased gradually at temperatures above 200 °C. This phenomenon is due to the desorption of chemically absorbed water and decomposition of functional groups on the graphene surface. The weight loss experienced by G1 and TRG2 at 600 °C is 11 and 14%, respectively. The fact that the weight loss is 3% greater in the case of TRG2 can be attributed to two reasons: (1) TRG2 having higher aspect and surface area-to-volume ratios, which means that it might have more water adsorbed to it via hydrogen bonds than G1 and (2) TRG2 having higher COOR, lactone, and anhydride content than G1. The amount of grafting was calculated based on the weight difference in the residue at 600 °C between the unfunctionalized (G1 and TRG2) and functionalized (Modi-G1 and Modi-TRG2) graphenes. In Figure 3, it is seen that Modi-G1 and Modi-TRG2 experienced 4 and 6% more weight loss than G1 and TRG2, respectively, which may be explained by (1) a general rise in the amount of trimellitic anhydride tethered to the graphene surface postfunctionalization and (2) Modi-TRG2 containing more trimellitic anhydride groups than Modi-G1. Scheme 1 shows that trimellitic anhydride groups occur in the functionalized graphenes at the rates of 1 group/340 carbon atoms in Modi-G1 and 1 group/240 carbon atoms in Modi-TRG2.

**Dispersibility and Interface Morphology of the PET/Graphene Nanocomposites.** The morphology of the melt-mixed PET/graphene composites was analyzed using TEM and used to compare dispersibility for the functionalized graphenes (Modi-G1 and Modi-TRG2) versus the unfunctionalized graphenes (G1 and TRG2). The TEM images of PET/graphene nanocomposites are shown in Figure 4. Both G1 and Modi-G1 seem well-dispersed in PET, although some aggregates were observed. On the other hand, there appears to be significant differences in dispersibility between TRG2 and Modi-TRG2 (Figure 4c–e). The dispersion of TRG2 in the PET matrix is inhomogeneous; there are visible variations in concentration of graphene in PET/TRG2 (Figure 4c,d), whereas Modi-TRG2 is well-dispersed in its PET matrix (Figure 4e,f). PET/Modi-TRG2 nanocomposites are dispersed to a few-layer thickness, indicating that Modi-TRG2 has an enhanced dispersibility in PET compared with TRG2 but with graphene sheet edges that are wrinkled and twisted in the case of the former.
The electrical resistances of the nanocomposites are depicted in Figure 5. As expected, all the PET/graphene nanocomposites experience significant reductions in electrical surface resistance compared with the pure PET. However, the different graphenes vary greatly in percolation onset, about 4 wt % loading for G1 and Modi-G1 (Figure 5a) and 1 wt % for TRG2 and Modi-TRG2 (Figure 5b). Additionally, the surface resistance of PET/Modi-TRG2 at 1 wt % is slightly lower than that at 0.5 wt %, whereas that of PET/TRG2 remains the same even as the TRG2 loading increases from 0.5 to 1 wt %. The TEM results shown in Figure 4c-f support the notion that PET/Modi-TRG2 can conduct electricity better than PET/TRG2 composites around the percolation concentration, by virtue of the more homogeneous dispersion of graphene in PET in the case of the former. For circular disks oriented randomly within a polymer matrix, the percolation onset limit \( A_{t} = D/h = 3\Phi_{spher}/2\Phi_{per} \), as shown in eq 1\(^{48}\)

\[
A_{t} = \frac{D}{h} = \frac{3\Phi_{spher}}{2\Phi_{per}}
\]

where \( \Phi \) is the volume fraction of the filler, \( \Phi_{spher} (=0.29) \) is the percolation threshold for randomly packed spheres, and \( \Phi_{per} \) is the percolation threshold for circular discs.\(^{60}\)

In calculating the volume fraction for the graphene filler, the values of densities used were 2.28 g/cm\(^3\) for graphene\(^{19,20}\) and 1.335 g/cm\(^3\) for amorphous PET [crystallinity by differential scanning calorimetry (DSC) was below 5% for all samples, as shown in Figure S3 of the Supporting Information].\(^{25,46}\)

The calculated value of \( A_{t} \) is 20 for G1 and Modi-G1 and around 80 for both TRG2 and Modi-TRG2. Thus, TRG2 is estimated to have an aspect ratio four times that of G1 (and the same applies for Modi-TRG2 vs Modi-G1).

**Nanocomposite Melt Rheology.** Melt rheology was measured for all nanocomposite samples to better understand
the graphene dispersion levels\textsuperscript{20,61} and the degree of molecular networking\textsuperscript{62} within each system. Figure 6 shows dynamic strain sweeps conducted at 1 rad/s for all samples, demonstrating an increase in elasticity as a function of graphene volume fraction typical of such systems of graphene nanocomposites.\textsuperscript{20,63} It is observed that the $G'$ for the PET/filler nanocomposites increases more at lower graphene loadings than for the corresponding unfunctionalized nanocomposites. All nanocomposite systems demonstrate yield behavior at high values of strain, with $G'$ dropping sharply at strains above the critical strain, $\gamma_{\text{crit}}$. Moreover, it is noticed that $\gamma_{\text{crit}}$ shifts to lower values as the graphene loading increases, a characteristic of fragile filler network formation.\textsuperscript{20} Figure 7 depicts how $\gamma_{\text{crit}}$ varies as a function of filler loading.

$\gamma_{\text{crit}}$ experiences a sharp drop when the volume fraction of graphene becomes approximately 0.025 (4 wt %) for G1, 0.049 (8 wt %) for Modi-G1, between 0.006 (1.0 wt %) and 0.012 (2.0 wt %) for TRG2, and between 0.003 (0.5 wt %) and 0.006 (1.0 wt %) for Modi-TRG2. These volume fractions imply the percolation of a graphene network. Both dispersion uniformity and fragility of the graphene network are similar for the G1 and Modi-G1 composites based on the melt rheology evidence. On the other hand, $\gamma_{\text{crit}}$ of Modi-TRG2 occurs at a lower concentration than that of TRG2, indicating that Modi-TRG2 is better dispersed in its PET matrix than TRG2, which is consistent with the observations based on the TEM images and the electrical conductivity results.

Figure 8 shows the results of dynamic frequency sweeps conducted on the nanocomposite samples, demonstrating an initial increase in $G'$ at lower frequencies $\omega$ as a function of filler loading across all samples, until the loading reaches a critical value, following which the response becomes independent of $\omega$. This observed trend is a solid-like behavior normally displayed by nanosheet-laden polymer nanocomposite melts (e.g., polymer/graphene)\textsuperscript{20,48,58,64–66} as it is a
signature of the formation of networks of filler–filler contacts. It is also observed that the rise in $G'$ of PET/Modi-G1 over the low frequency range is marginally higher than with the PET/G1 system, while that for PET/Modi-TRG2 at low frequencies is much bigger than that for PET/G2. Figure 9 depicts the behavior of $G'$ at a frequency $\omega = 0.1$ rad/s for all nanocomposite samples as a function of graphene loading. It may be observed that the PET/Modi-G1 system displays a greater $G'$ than PET/G1 for graphene loadings below the percolation limit $\Phi_{\text{per}}$ ($\Phi < 0.025$, <4 wt %). At the same time, Modi-TRG2 was observed to display greater $G'$ than TRG2 at all graphene loadings from 0.003 (0.5 wt %; under $\Phi_{\text{per}}$) to 0.012 (2 wt %; above $\Phi_{\text{per}}$), so the enhancement achieved via graphene loading is more pronounced with TRG2 than for

Scheme 2. Reaction between Modified Graphene and PET
Modi-TRG2. This preceding observation may be explained as follows: Modi-G1 and Modi-TRG2 are both surface-functionalized with trimellitic anhydride, which provides potential esterification sites for the hydroxyl and carboxy groups on PET chains and can lead to chemical network formation and cross-linking during the melt processing (see the Supporting Information, Scheme S2, reaction I and II).55 In particular, this coupling of PET is known to confer a stronger elastic character and greater values of $G'$ compared with linear PET.46 Here, the number of functional groups in Modi-TRG2 is more than that in Modi-G1, meaning that the coupled network in PET/Modi-TRG2 is denser than that in PET/Modi-G1. As a result, PET chains in PET/Modi-TRG2 composites are more geometrically restricted in terms of mobility than in PET/Modi-G1 composites, and thus, the composite melts of the former show lower liquidity as a result of functionalization (Scheme 2).

Mechanical Properties of PET-Based Nanocomposites. Figure 10 depicts both Young’s modulus and elongation at break of the nanocomposites. As expected, an enhancement effect is observed in Young’s modulus across nanocomposite systems compared with the pure PET (Figure 10a,b): for the G1 systems, 4 wt % of filler loading leads to a Young’s modulus increase of 4% for PET/G1 and 12% for PET/Modi-G1, while for the TRG2 systems, 2 wt % loading causes 13% modulus increase for TRG2 and 18% for Modi-TRG2. It is thus generally observed that the inclusion of functionalized graphene causes approximately 5% incremental rise in Young’s modulus of the nanocomposites compared with the non-functionalized graphenes. The elongation at break for all nanocomposite systems dropped as a function of graphene loading. Elongation at break of PET/TRG2 and PET/Modi-TRG2 was similar with concentrations from 0.5 to 2.0 wt %, whereas PET/Modi-G1 displayed greater elongation at break than PET/G1 at loadings 1.0–4.0 wt %. Figure 11 depicts the dependence between Young’s modulus and elongation at break across nanocomposites.

It is observed from the figure that PET/G1 experiences a sharp drop in the elongation at break, followed by a small increase in Young’s modulus, which was already demonstrated in a prior work.46 PET/TRG2 showed lower elongation than PET/G1 at lower graphene loadings but increased Young’s modulus with an increase in graphene loading. By comparison,
Modi-G1 is observed to cause a suppression of the drop in elongation at break in its PET nanocomposites, while Modi-TRG2 was found to enhance Young’s modulus in PET/Modi-TRG2 composites. The preceding observations indicate that the modified graphenes have a marked effect on improving Young’s modulus of composites in the case of the higher-aspect ratio Modi-TRG2, while they suppress the decrease of elongation in the case of the lower-aspect ratio Modi-G1.

Enhancement Mechanism of Mechanical Properties. The preceding set of observations leads us to propose an explanatory model for the mechanical property enhancement of the functionalized graphenes on the PET/graphene nanocomposites. As described in our previous study, PET/low $A_f$ graphene nanocomposites can be plastically deformed, with the grafted PET chains on Modi-G1 enhancing interfacial adhesion with the polymer matrix during melt-processing and forming a coupled network while maintaining a similar overall level of dispersibility. Stronger interfacial adhesion results in high stress transfer efficiency from the PET matrix to the graphenes, and the coupled network which is formed suppresses both strain-induced orientation and strain-induced crystallization during deformation of the nanocomposites, resulting in additional enhancement both of Young’s modulus and elongation at break over nanocomposite samples prepared using unmodified G1. The same functionalization conducted on a higher-aspect ratio graphene revealed a different trend: the higher aspect ratio and specific surface area of TRG2 cause it to disperse inhomogeneously in the PET matrix with lower interfacial adhesion prior to functionalization, resulting in a minor improvement effect of mechanical properties of the PET-based nanocomposites. On the other hand, Modi-TRG2 enhances dispersion homogeneity via enhancement of graphene wettability and dispersibility in the PET matrix by grafted PET chains. Additionally, PET/Modi-TRG2 forms stronger interfaces and a denser network. The stronger interfacial adhesion in functionalized graphenes (especially, Modi-TRG2) stabilizes the interface formed between the PET matrix and graphene while improving stress transfer efficiency between the two, leading to an additional enhancement in Young’s modulus of the nanocomposites as a result of using the functionalized high-$A_f$ graphene. The reason that PET/ Modi-TRG2 did not improve the elongation at break is thought to be the difference in filler size (aspect ratio) and mobility of PET chains. The PET chains in nanocomposites with higher-aspect ratio graphenes are more geometrically restricted than chains in composites of the lower-aspect ratio graphenes. These PET chains can be normally pulled off from an entanglement of PET chains during deformation and the deformation energy is absorbed during the unentanglement process, resulting in plastic deformation. However, this is not allowed in the cases of the TRG2 and Modi-TRG2 composites because of stronger restrictions of the molecular chain by the higher-aspect ratio graphenes via chain confinement effects, which hinders PET chains from unentanglement during deformation, resulting in lower capacity to absorb deformation energy and thus brittle fracture. However, the denser coupled network and stronger interface adhesion in PET/Modi-TRG2 composites compared with PET/TRG2 lead to more effective stress transfer efficiency between PET and graphene. Therefore, the increase in the amount of surface modification is thought to be responsible for the drastic improvement in Young’s modulus of PET/Modi-TRG2 compared with PET/TRG2.

CONCLUSIONS

Trimellitic anhydride functionalization was conducted on two thermally reduced graphenes of different aspect ratios, $A_f$, and the same C/O ratio (8:1). The impact of this functionalization was studied on improving the dispersion quality of melt-mixed nanocomposites of graphene and PET. Nanocomposites with low-$A_f$ graphene (PET/G1 and PET/Modi-G1) showed similar dispersion as shown both by melt rheology and electrical resistance. In this case, the grafted PET chains on Modi-G1 during melt-processing enhanced the interfacial adhesion and formed a coupled network, as a result of which strain-induced orientation and strain-induced crystallization were suppressed because of the presence of functionalized graphene, resulting to enhance Young’s modulus and higher elongation as reported in our previous study. On the other hand, the nanocomposites with higher $A_f$ graphene (PET/TRG2 and PET/Modi-TRG2) showed a different tendency, displaying a lower elongation at break than in composites of the lower-$A_f$ graphenes because of the difficulty in pulling off molecular chains in the case of the former. The PET/Modi-TRG2 composites formed a more homogeneous dispersion, stronger interfacial adhesion, and denser coupled networks than those of PET/TRG2 composites because of denser coupled network and stronger interfacial adhesion in PET/ Modi-TRG2 composites which lead to effective stress transfer efficiency between the PET and graphene, resulting in a drastic improvement in Young’s modulus. This was, however, not accompanied with a corresponding improvement in the elongation at break because of the higher geometrical chain restriction in the presence of the high-aspect ratio TRG2 graphene. The preceding observations demonstrate the potential impacts of tuning both surface chemistry and aspect ratio of graphene in the fabrication of PET/graphene composites.

EXPERIMENTAL SECTION

Materials. PET powder (30 mesh particle size, intrinsic viscosity 0.61 dL/g (in ortho-chlorophenol), used in our previous work) was produced by grinding the pellets [obtained from Toray Plastics America (North Kingstown, RI)] using PolyVision (Manchester, PA). Multilayered graphene was used as nanofillers. The thermally reduced graphenes, G1 (XG Science, xGnP-C750, thickness 2 nm, diameter $< 2 \mu m$, surface area $\sim 700 m^2/g$, used in our previous work), and TRG2 (Vorbeck Materials, produced by thermal exfoliation of GO produced via the Staudenmaier method, with a specific surface area of $\sim 800 m^2/g$). Anhydrous DMF (EMD Chemicals Inc.), anhydrous pyridine (Sigma-Aldrich), and 1,2,4-benzentriacarbonyl anhydride acid chloride (trimellitic anhydride acid chloride, AK Scientific, Inc.) were all used as received as per our previous work.

Surface Modification of Graphene. The surface functionalization of the graphene ( Modi-G1 from G1 and Modi-TRG2 from TRG2, respectively) was conducted following the same method published on our previous work.

Preparation of Nanocomposites with PET. The PET/unmodified or modified graphene nanocomposites were prepared by melt-blending, and thin samples for performing TEM and measuring electrical resistance and mechanical properties were prepared by melt-processing following the method used in our previous study. PET powder, unmodified or modified graphene, and the obtained nanocomposites were
vacuum-dried at 120 °C for more than 12 h prior to melt-pressing.

**Characterization.** Characterization of samples was conducted using following equipment. Detailed procedure and measurement parameters are reported elsewhere.\(^{46}\)

FT-IR spectra of graphene and modified graphene were collected using a Magna IR-750 spectrometer ( Nicolet Instrument, Madison WI) with the attenuated total reflection method.\(^ {49-53}\)

XPS of all graphenes (unfunctionalized/functionalized) were acquired via a Surface Science 555 instrument with Mg Kz radiation to understand the different bonding environments within the graphenes.\(^ {39-53}\)

Thermogravimetric analysis (TGA) of the graphenes was conducted via a PerkinElmer Pyris Diamond TG/DTA 6300 instrument.

Dispersion, intercalation, and exfoliation of graphene were all visualized via TEM using an FEI Tecnai T12 instrument with 120 kV as the accelerating voltage.

Surface resistance of nanocomposite films was measured using an 11-probe dc resistance meter (Prostat-801).

The rheology of the nanocomposite samples was measured using a strain-controlled rotational rheometer (ARES, TA Instruments) at 270 °C under an inert \( \text{N}_2 \) blanket.

DSC measurements were performed using a TA Instruments Q1000 to investigate the crystallinity of nanocomposite films. All measurements were carried out in a \( \text{N}_2 \) atmosphere.

The mechanical properties of the nanocomposite samples were measured using a rheometrics solid analyzer, RSA-G2 (TA Instruments, New Castle, DE).

**ASSOCIATED CONTENT**

1. Supporting Information

   The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03288.

   Proposed reaction schematic for grafting of the trimellitic anhydride group on graphene and PET, FT-IR spectra and XPS high-resolution scan of O 1s of graphenes, and crystallinity of amorphous PET-based nanocomposites sheets (PDF)

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**Notes**

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