

Synthesis and Characterization of Amphiphilic Reduced Graphene Oxide with Epoxidized Methyl Oleate

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Graphene oxide (GO) is an individual sheet of oxidized carbon atoms. As a result of its unique molecular and electronic construction, GO has exhibited excellent physical properties and great potential for exotic applications, but its strong hydrophilic nature limits its dispersibility in certain organic solvents and hinders its application, especially in the polymer composite area. Here we demonstrate amphiphilic, highly conducting molecular sheets of oleo-functionalized reduced GO (oleo-GO) produced by a solvent-free, one-pot synthesis that interfaces GO with epoxidized methyl oleate (EMO), a common, sustainable source for functionalized oleochemicals. This process is green, prevents waste, and has low toxicity because of the fatty acid esters. Furthermore, EMO's environmental benefits have been extensively reported through life cycle assessment. In this study, the hydroxy and carboxylic acid moieties of GO were converted into α -hydroxy-ethers or α -hydroxy-esters after opening the epoxide ring of EMO, and then partial annealing induced reduction of the oxy-groups on the internal surface of GO. This unique α -hydroxy functionalization enabled the oleo-GO to function as amphiphilic. As a result, the oleo-GO was successfully dispersed in various organic and water-miscible solvents. We propose a chemical structure and a chemistry route for the oleo-GO functionalization by X-ray photoelectron spectroscopy (XPS), NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and Raman spectroscopy. Transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM) provided structural characterization of the oleo-GO sheets. Thermogravimetric analysis (TGA) of

the oleo-GO exhibited a thermo-degradation pattern similar to reduced GO, but different from GO and thermally annealed GO. In addition, we demonstrate stable dispersions of oleo-GO in poly(lactic acid), a biopolymer, with mechanical reinforcement.

Lipids are a main component of plants and are a readily usable renewable resource.^[1,2] Recently, researchers have found a broad range of applications for functionalized lipids as additives for plastics,^[3] hydrogels,^[4] and lubricants.^[5] Epoxidized lipids such as EMO are inexpensive, commercially available, and act as sustainable raw materials. In this study, we employed EMO to functionalize GO to make it amphiphilic. Graphite is abundant in nature and graphene sheets (single-atom-thick sheets of sp^2 hybridized carbon atoms) have received great interest since their successful isolation and characterization,^[6] which led to the 2010 Nobel Prize in Physics. Chemical oxidation methods have been the most common approach used to exfoliate graphite into GO.^[7,8] GO has gained attention because of its high mechanical strength, which provides reinforcement, and its functionalizable oxy-groups, low cost, and wide availability.^[7,8] Dispersions of GO can be reduced to produce reduced graphene oxide (rGO), which has a significantly high sp^2 character with improved mechanical, thermal, chemical, electrical, and optical properties compared with GO;^[9–15] however, GO has limited solubility. It is dispersible in water and some high-boiling-point organic solvents (e.g., DMF and ethylene glycol) that are not favorable in polymer composite applications because removing or recycling these high-boiling-point solvents requires more energy. Homogeneously dispersing rGO in organic solvents has been a challenge for practical applications of graphene-based materials for polymer-based composite applications.^[13,16–18] The dispersibility of GO in various organic solvents has been investigated,^[19,20] and several trials have been accomplished with chemical modifications:^[21] non-covalent^[22] and covalent functionalization^[23] with various materials and polymers such as octadecylamine,^[24] perfluorophenylazide,^[25] poly(vinyl alcohol)^[23] and aryl diazonium salts,^[26] poly(ethylene glycol),^[27] polyethylene-block-poly(ethylene oxide),^[28] and polystyrene.^[29]

In addition, amphiphilic graphene composites were obtained by π - π interactions with coil-rod-coil conjugated triblock copolymers^[17] and polyphenols from green tea extract,^[30] poly(phenylene methylene).^[31] In addition, GO was utilized to facilitate chemical reactions as sustainable heterogeneous carbon catalysts^[32] such as for the oxidation and hydration of alcohols,^[33] as efficient oxidants,^[34,35] and as an auto-tandem oxidation-hydration-aldol coupling catalyst.^[36]

Because of stricter environmental regulations and growing awareness about sustainability,^[37,38] greener approaches for reducing GO have received significant attention. Tech-

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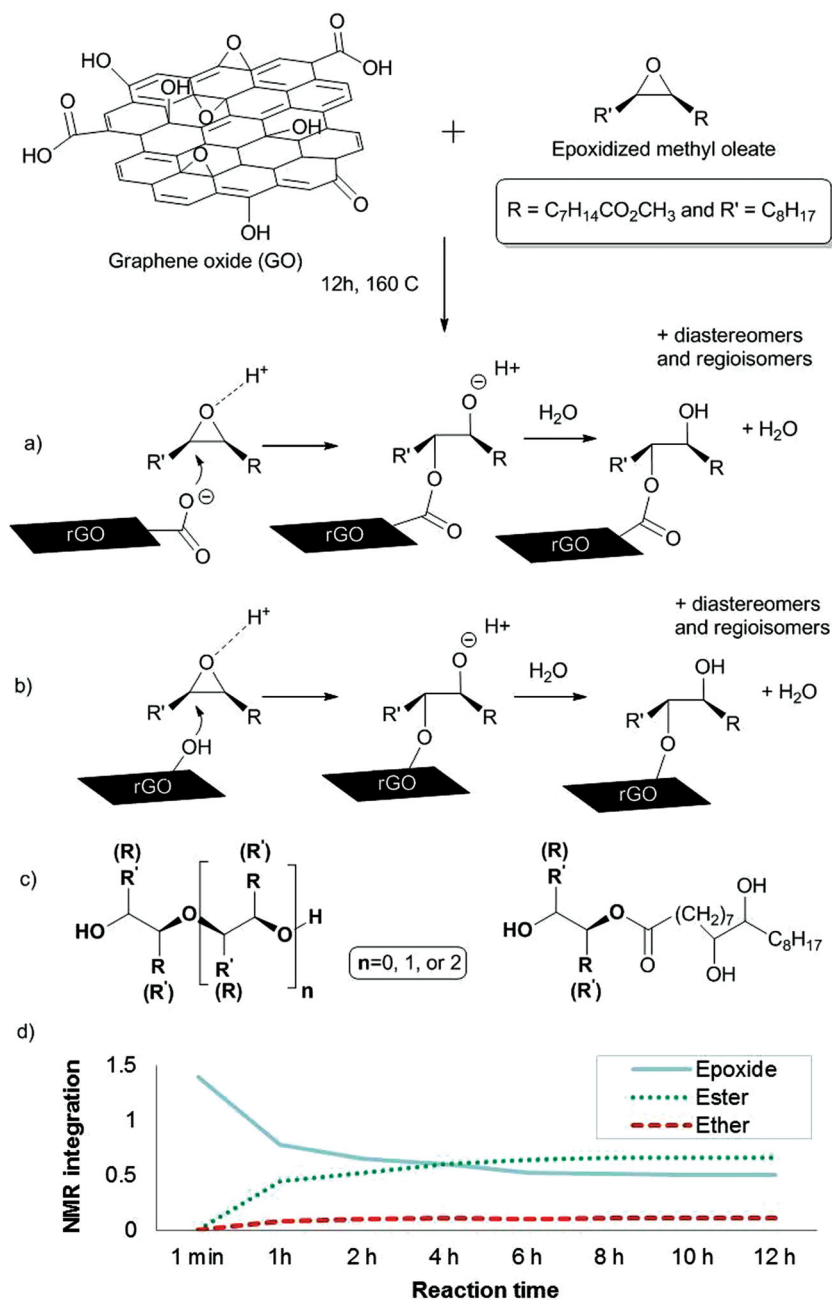


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niques have included the use of alcohols,^[39] melatonin,^[40] microwave,^[41] microbes,^[42] tea extract,^[30] and sodium hydride.^[43] In this study, we synthesized oleo-GO using EMO by a solvent-free and catalyst-free, one-pot process at 160 °C overnight. The hydroxy and carboxylic acid groups on GO were not only functionalized by mid-chain α -hydroxy-etherification and -esterification of EMO, but also reduced through the annealing process.^[12] This oleo-GO was able to disperse in several low-boiling-point organic and water-miscible solvents because of its unique amphiphilic nature that evolved from the mid-chain α -hydroxy-formation. Our green process without organic solvents ensures low toxicity, enhanced atom economy, and waste prevention. Selective functionalization can serve as a precursor for further modification of GO to convert it into an opto-electronic material by chemical or thermal reduction.^[11,44] More importantly, our amphiphilic oleo-GO is a meaningful contribution to the field of polymer composites because of its dispersibility in a wide range of solvents, especially in greener media such as ethanol and ethyl acetate,^[45] which is relevant in developing feasible manufacturing routes for graphene-based nanocomposites.^[46]

Poly(lactic acid) (PLA) was chosen as a matrix for green oleo-GO-based nanocomposites to demonstrate oleo-GO's applicability in future high-performance biopolymers. PLA is one of the most promising bio-based, renewable resource-derived thermoplastics in that it has the potential to replace several conventional petroleum-based polymers.^[47,48] However, some of its unsatisfactory characteristics, such as moderate modulus and strength, low thermal stability, and poor gas barrier properties, have limited its broad application. In the last two decades, polymeric nanocomposites have emerged as a means to alter the thermal, mechanical, and processing characteristics of pristine polymers.^[49,50] In particular, PLA-based nanocomposites have been reported in conjunction with various nanoparticle systems, including carbon nanotubes, graphite, layered silicates or clays, silica, polyhedral oligomeric silsesquioxane, magnesium oxide, titanium oxide, etc.^[51–56] In this study, we investigate oleo-GO's potential as a reinforcing agent for PLA.

Because GO has carboxylic acid units and phenolic OH groups, the connectivity was envisioned from the reaction of these functional groups with epoxides from EMO. Indeed, our group (Biomaterials and Technology Lab) and others have previously reported the successful ring opening of EMO with carboxylic acids or secondary (aliphatic) alcohols with concomitant formation of ester or ether linkages.^[57–64] To manifest



Scheme 1. Proposed chemical pathway of a) α -hydroxy esterification of carboxylate, b) α -hydroxy etherification of hydroxy, and c) by-products of ether- and/or ester cross-linked oligomers of EMO. d) NMR integration using a methyl group (δ 0.88) as a quantitative internal standard.

quantitatively the degree of epoxide couplings with GO-carboxylic acids on the one hand and with GO-phenolic groups on the other hand, we used a model system of benzoic acid (1 equiv.), phenol (1 equiv.), and epoxidized methyl oleate (3 equiv.) as a nucleophilic competition experiment. Conversions and yields were determined by ¹H NMR integration with the oleo-terminal methyl signal (3H, triplet at δ 0.80) as an internal standard (Figure S1, Supporting Information) while monitoring the reaction from 1 min through 12 h at 160 °C (Scheme 1d). After 1 h and 68 ± 4% conversion of the epoxide, we obtained a 44 ± 4%

yield of the ester (from carboxylic acid addition) and a $16 \pm 2\%$ yield of the ether (from phenol addition) with a 2.75-fold bias in favor of carboxylic acid attack. This result was in agreement with a previous study that reported the nucleophilicity of octanoic acid was roughly 4–5 times more reactive than phenol under neutral conditions at high temperature (i.e., $160\text{ }^{\circ}\text{C}$).^[65] The clean ring-opening reaction by benzoic acid/phenol resulted in no discernible cleavage of the methyl ester ($\delta\text{ }3.65$) from hypothetical transesterifications or saponifications even after 12 h.

These studies underline that available functional groups in GO (carboxylic acids and phenolic units) are generally capable of cleanly forming two types of covalent linkages with epoxy-groups in EMO at elevated temperatures. The oxirane ring opening is possibly an acid-catalyzed process in which carboxylates act as the active nucleophiles (Scheme 1).

Heating a mixture of GO with a large excess of EMO at $160\text{ }^{\circ}\text{C}$ for 12 h produced a new material (oleo-GO) that was characterized by a 10% weight uptake from GO after the addition of hexane and centrifugation of the suspension. Oleo-GO was well dispersed in CDCl_3 , thus allowing ^1H NMR analysis. Oleo-GO's particular fatty acid NMR pattern [alkyl (CH_2), Supporting Information]. The ^1H and ^1H - ^1H COSY NMR spectra of the EMO by-product after the process showed α -hydroxy-ester [$\text{RR}'\text{C}(\text{H})\text{O}$ -ester signal at $\delta\text{ }4.85$ and vicinal alcohol signal at $\delta\text{ }3.6$] and α -hydroxy-ether [$\text{RC}(\text{H})(\text{OH})\text{C}(\text{H})(\text{R}')\text{O}$ -ether at $\delta\text{ }3.55$ and vicinal alcohol signal at $\delta\text{ }3.2$ and 3.1], verifying that both acids and phenolic OH groups from GO have established covalent bonds to EMO by epoxide ring opening. The vicinal alcohol signal at $\delta\text{ }3.6$ was not clearly shown because of a strong ether signal around $\delta\text{ }3.55$, but the signals of the α -hydroxy-ester and α -hydroxy-ether were confirmed in our previous study.^[58] Because EMO was applied in large excess relative to GO, it was not surprising that oligomerized EMO had formed as a side product (Figure S2, Supporting Information).^[58,64] ESI-MS confirmed 1–3 units (mono-, di-, and trimer) of EMO oligomers (Figure S3, Supporting Information). Such oligoethers have been reported to have potential applications as biolubricants with antioxidative properties.^[66,67]

The oleo-GO was well dispersed in ethanol, acetone, ethyl acetate, methanol, and the 90:10 mixture of water and ethanol (v/v), but precipitated in hexane and dichloromethane (lower polarity) after 30 min without agitation (Figure 1a–c). Ethanol is one of the desirable organic solvents for polymer composite applications because of its low toxicity, low greenhouse gas emissions, and low energy input.^[68] We suggest that the combination of polar α -hydroxy ester/ α -hydroxy ethers coupled with unpolar alkyl chains provides an amphiphilic environment that allows for solubilizing interactions with a wide range of solvents, and that combination also counteracts shriveling of the GO nanosheet (Figure 1d,e).

Interestingly, the solutions of oleo-GO are black in appearance, which suggests a deoxygenation (or reduction) and at least partial rearomatization of GO.^[43] This may be explained at least to some extent by an effective dehydration of the GO core through epoxide hydrolysis of EMO to form a 9,10-diol. Such a compound would, in turn, explain the occurrence of EMO oligomers, because we have previously found that diols initiate the oligomerization process of EMO.

The XPS (Figure 2a–e) C 1s and O 1s spectra were curve-fit using Gaussian–Lorentzian functions with a Shirley background correction. The expected spacings of +0.0, +1.5, +2.5, and +4 eV were used to curve-fit the C 1s spectrum for C–C, C–O, C=O, and O=C–OH, respectively (Figure 2a–d). The C–C peak appears at 285.7 eV for GO and 285.0 for oleo-GO, and the GO spectra were not shifted to account for surface charging. Three peaks were assigned to GO O 1s with optimized positions at 532.7, 533.6, and 534.4 eV, corresponding to C–O, C=O, and C(=O)OH, respectively (oxy-groups on GO). Two peaks were assigned to the oleo-GO O 1s spectra, with optimized positions at 532.5 and 533.7 eV. The intensities of the C 1s and O 1s curve-fit analysis indicate a partial reduction of C–O and an extensive reduction of C=O after the oleo-functionalization of GO. This was also confirmed by Raman spectroscopy (Figure 3a,b) by an optical spectrometer connected with a 532 nm laser excitation. To independently confirm the oleo-functionalization of GO according to Scheme 1a,b by XPS, we synthesized fluoride-labeled oleate (9,10-epoxidized p-fluorobenzyl oleate), which was subsequently annealed to GO. The XPS fluoride signal in this fluoridated oleo-GO is clearly shown in Figure 2 e; the composition of fluoride/carbon was quantitatively 2% in this system.

Papers made by filtering GO and oleo-GO were examined under a Raman microscope. The I_D/I_G ratio is used as a measure to determine the extent of sp^3 hybridized carbons. The I_D/I_G for GO (~ 1) is 25% higher than that for oleo-GO (0.8), indicating a significant increase in the sp^2 graphenic region of the oleo-GO. In addition, the TGA showed that oleo-GO is significantly more thermally stable than pure GO and more thermally stable than oven-annealing GO in the temperature range of $<200\text{ }^{\circ}\text{C}$ and $>570\text{ }^{\circ}\text{C}$. This suggests a more robust and partially aromatized core that is less prone to loss of oxygenated small molecules from fragmentations. The fact that oven annealing of GO does not diminish the TGA weight loss until temperatures above $700\text{ }^{\circ}\text{C}$ rules out any potential thermal stabilization from heating oleo-GO during the reaction with EMO (Figure 3c).

The sheet resistance of GO ($1188\text{ M}\Omega\text{ sq}^{-1}$) was 33-fold more than that of oleo-GO ($36\text{ M}\Omega\text{ sq}^{-1}$) (Figure S8, Supporting Information). The significant increase in conductivity in oleo-GO confirms that additional conjugated π -electrons (charge carriers) were generated during the formation of oleo-GO after treatment with EMO.

The tensile bars of PLA/GO composites are shown in Figure 4a. PLA exhibited a tensile strength of 72.2 MPa and a Young's modulus of 1.8 GPa. With the addition of 1% oleo-GO, the tensile strength and Young's modulus increased to 76.8 MPa and 2.2 GPa, respectively (Figure S9, Supporting Information). The storage modulus of PLA was only about 0.98 GPa before glass transition, whereas that of PLA/oleo-GO was 2.3 GPa, which was more than two-fold larger than PLA (Figure S10, Supporting Information). The hydrophobic interactions between oleo-GO and PLA (Figure 4) enhanced the mechanical strength of the composites whereas GO/PLA composites underwent severe pyrolysis, which resulted in brittle and broken tensile bars.

During glass transition, the storage modulus of both PLA and PLA/oleo-GO dropped sharply, and increasing the temperature

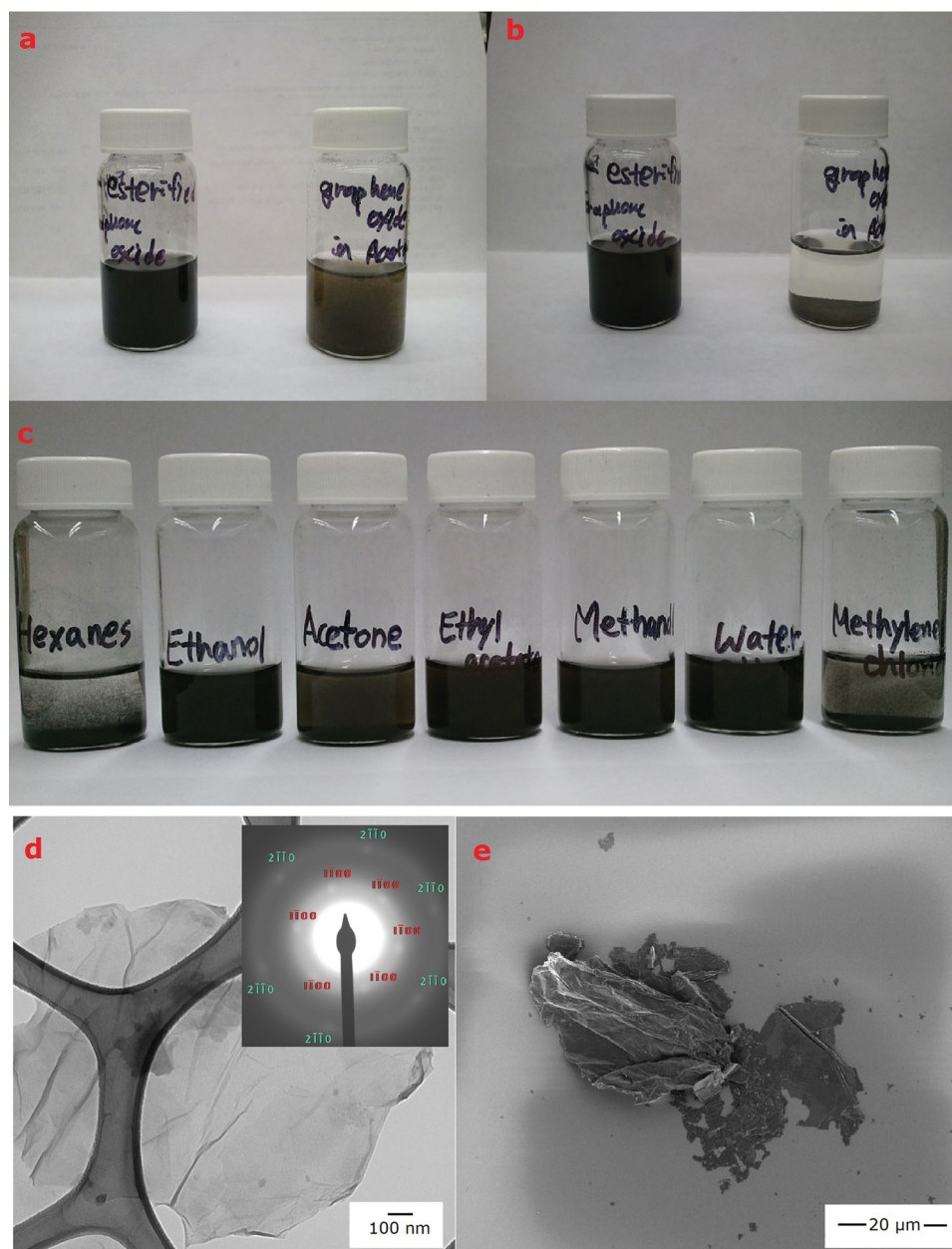


Figure 1. a) Oleo-GO and GO in acetone immediately after sonication for 5 min, b) oleo-GO and GO in acetone 30 min after sonication, c) dispersibility of oleo-GO in (left to right) hexanes, ethanol, acetone, ethyl acetate, methanol, water-miscible solvent [water:ethanol (90:10 v/v)], and dichloromethane 30 min after 5 min sonication, d) TEM of oleo-GO, e) FESEM of oleo-GO.

above the glass transition temperature led to a dramatic increase in the storage modulus, which was attributed to the cold crystallization of PLA. Moreover, the storage modulus increment of PLA/oleo-GO (2.3 GPa at 50 °C and 9.0 GPa at 125 °C, 6.7 GPa increment) was much larger than that of PLA (1.0 GPa at 50 °C and 4.1 GPa at 125 °C, 3.1 GPa increment), indicating that oleo-GO acted as a nucleating agent in the formation of PLA crystallites and thus increased the crystallinity. DSC results further confirmed such crystallization phenomena (Figure S11, Supporting Information). The heat of

crystallization and heat of melting of PLA were only 4.6 and 5.6 J g⁻¹, respectively, but those of PLA/oleo-GO were 10.6 and 10.9 J g⁻¹.

In summary, we have developed a novel amphiphilic reduced GO functionalized with epoxidized methyl oleate (renewable feedstock) by a green process. The solvent-free, one-pot esterification and etherification exhibited 99% conversion in the model system of benzoic acid and phenol. The benzoic acid was more nucleophilic than phenol, with secondary epoxides on the fatty acid mid-chain in the reaction, which could result

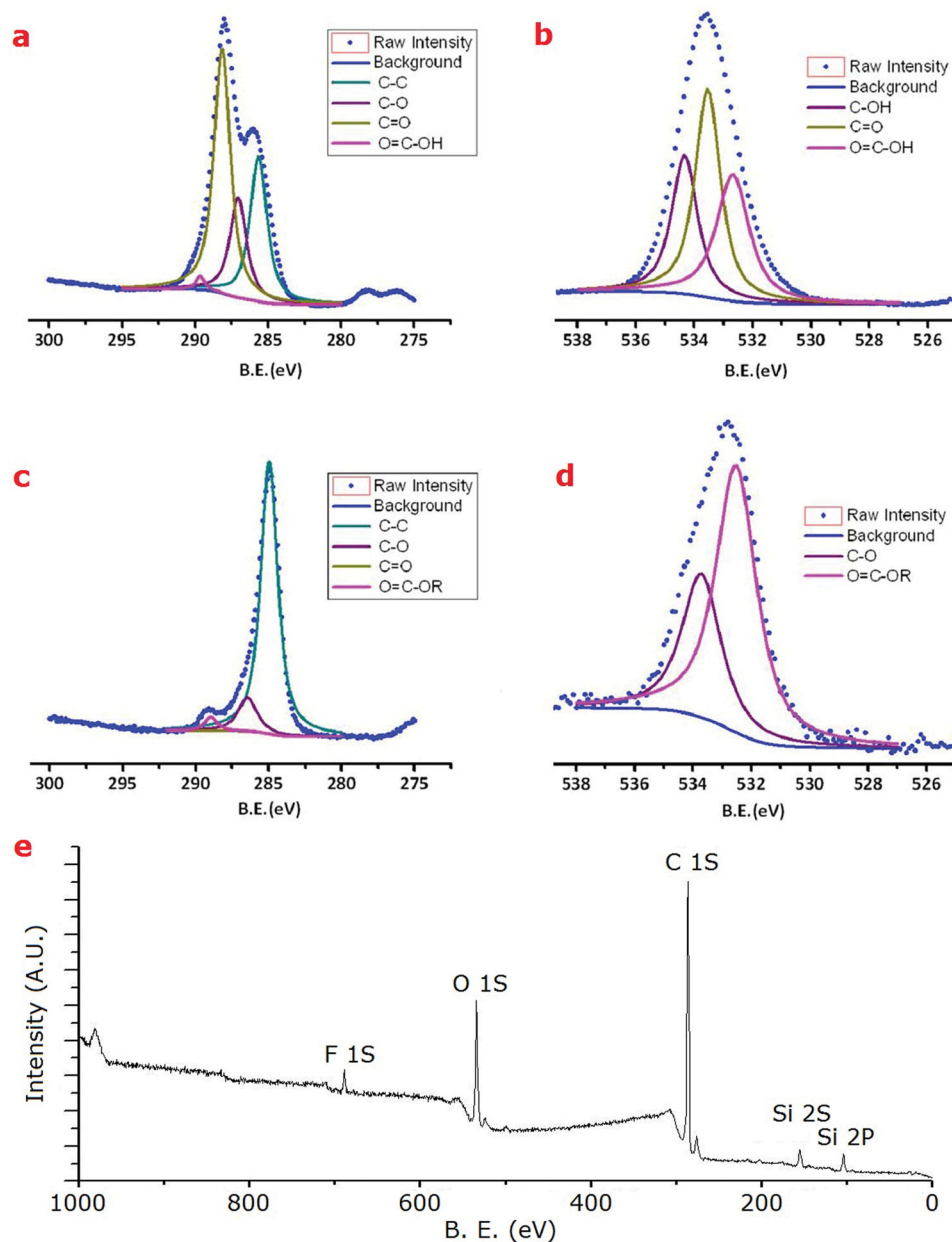


Figure 2. XPS spectra and peak fittings of a) GO C 1s, b) GO O 1s, c) oleo-GO C 1s, d) oleo-GO O 1s, and e) fluoride-labeled oleo-GO on a silicon wafer substrate.

in more ester formations than ethers in identical reaction conditions between GO and EMO. In addition, the by-product (oligomerized EMO) has shown excellent potential for bio-lubricant applications. We suggest that the significantly diverse solvent-dispersivity of oleo-GO and its controllable chemistry will provide an entry for industrially viable processes to produce future graphene-based polymer composites and systems. To prove this concept, we produced oleo-GO/PLA composites that are sustainable and economical. The oleo-GO nanocomposite presented excellent dispersivity of the graphenic sheets in the polymer matrix and significant improvement in mechanical properties.

Experimental Section

GO sheets suspended in deionized (DI) water were synthesized from mesh 7 graphite flakes (Sigma-Aldrich) by a modified Hummers acid oxidation method,^[69] which produced one- to four-atom-thick sheets of partially oxidized graphene. To obtain pure GO, the GO suspension was kept for 24 h, and then the middle layer (clear yellowish brown) was collected using a pipette and washed with DI water by centrifugation (10 000 rpm) for 60 min at 20 °C. This process was repeated until the pH of the DI water indicated neutral.

EMO was obtained from methyl oleate purchased from Fisher Scientific (Pittsburgh, PA) using the method from our previous reports.^[58,70,71]

GO (100 mg) was soaked in EMO (2 g), and then agitated at 160 °C for 12 h under solvent-free conditions. The solution was centrifuged (15 000 rpm)

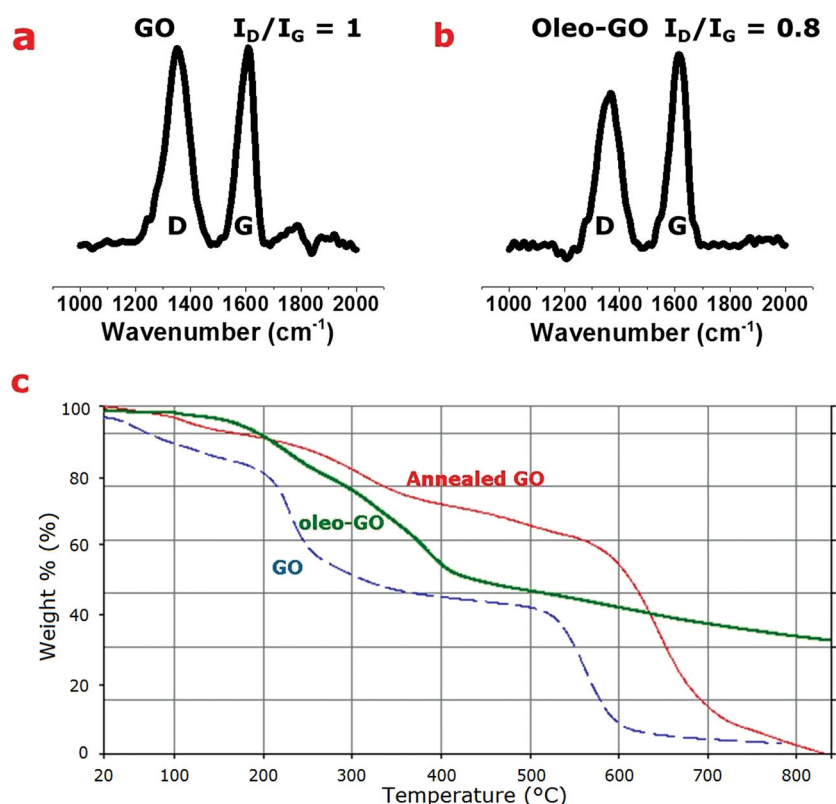


Figure 3. Raman spectra of a) GO and b) oleo-GO. c) TGA of GO, oleo-GO, and annealed GO.

for 45 min with hexane (350 mL) 3 to 5 times until the solution turned clear. After rotary evaporation, the hexane was recycled and the residue was collected and then vacuum-dried overnight. Oleo-GO (black powder) was recovered (110 mg), and further analyses were conducted.

Detailed information of experiments involving TEM, FESEM, Raman, conductivity tests, and oleo-GO/PLA nanocomposites are provided in the Supporting Information.

EMO was labeled with halogen (fluoride) for XPS analysis to clarify the oleo-functionalization of GO. 4-Fluorobenzyl alcohol was chosen to label EMO instead of aliphatic species because of its availability, straightforward incorporation into the ester moiety, and the preparative convenience of its UV activity during TLC sampling and the relative ease of NMR analysis of a *para*-substituted aromatic system. Because the ester group is far away from the epoxide, it was expected that the nature of a given ester alcohol would not really affect the reactivity of the epoxide. Prior to oleo-reduction of GO, *p*-fluorobenzyl alcohol (2.50 g) and oleic acid (3.70 g) were reacted at 75 °C overnight, and then *p*-fluorobenzoic oleate (5.15 g, 99% yield) was obtained as a brown liquid without purification. Subsequently, *p*-fluorobenzoic oleate (5.15 g) was reacted with *m*-CPBA (3.41 g) in dichloromethane (120 mL) at a temperature from 0 °C through to room temperature overnight. The mixture was extracted with saturated sodium metabisulfite (120 mL) and saturated sodium bicarbonate (120 mL), and the product purified by column chromatography (silica; hexane/ethyl acetate 99:1 to 80:20 gradient), to obtain 9,10-epoxidized *p*-fluorobenzyl oleate (3.7 g, 67% yield) as a white powder that melted at around 100 °C. ^1H NMR, ^{13}C NMR, ^{19}F NMR (Figure S6, Supporting Information) and high-resolution ESI-MS (Figure S7, Supporting Information) analyses confirmed its chemical structure.

To shed light on the nucleophilic competition between benzoic acid and phenol with EMO, EMO (2.98 g), benzoic acid (0.39 g), and phenol (0.30 g) in a molar ratio of 3:1:1 were agitated and aliquots (0.01 mL) were taken for NMR and ESI-MS analyses at 1 min, and 1, 2, 4, 6, 8, 10, and 12 h.

Detailed information of experiments involving TEM, FESEM, Raman, conductivity tests, and oleo-GO/PLA nanocomposites are provided in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley online Library or from the author

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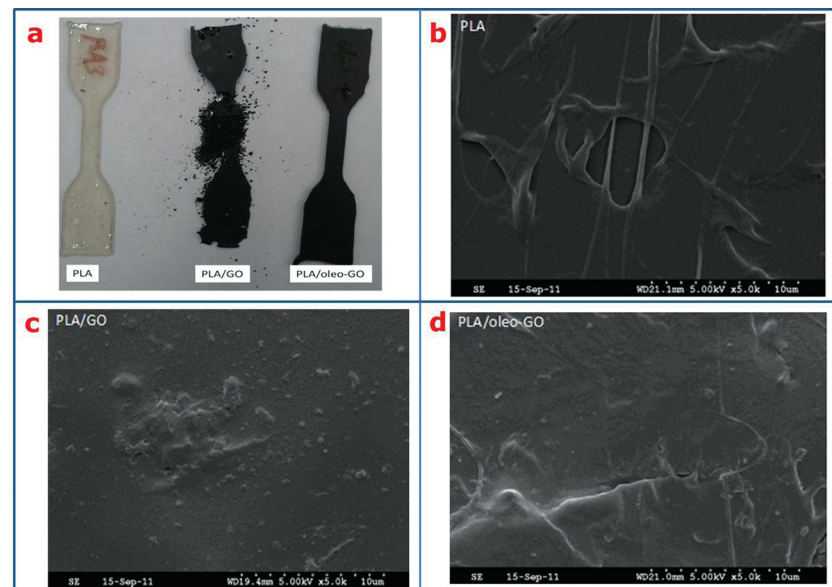


Figure 4. a) Images of PLA, PLA/GO, and PLA/oleo-GO composites (left to right) for the tensile test. The SEM images are of the fracture surface of PLA (b), PLA/GO (c), and PLA/oleo-GO (d) composites.

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