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INVITED REVIEW PAPER

Polymer/graphene oxide (GO) thermoset composites with GO as a crosslinker

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Abstract−Composites have historically been of intense interest due to their potential to replace glass, wood and metal at a fraction of the weight. Of the many choices of fillers, graphene oxide (GO) is generally attractive for its versatility and tunability in terms of surface functionality, size and shape. While the majority of GO has been incorporated into polymers and polymer precursors by physical mixing, this review focuses on research where GO has served as both a property enhancer and multifunctional crosslinker in thermosets. Methods for preparing GO (with and without additional functionalization) and incorporating it appropriately into thermosets are described. A review of characterization techniques, typically applied before and after GO is incorporated into thermosets and analytical methods for confirming important chemical reactions during crosslinking, is also provided. Finally, the resulting composite thermoset properties are surveyed throughout to connect preparation and characterization methods to their potential practical importance.

Keywords: Graphene Oxide, Polymer, Thermoset, Elastomer, Crosslinker, Epoxy

INTRODUCTION

In the past several decades, significant research effort has been devoted to polymer composites [1]. The general strategy of enhancing physical and chemical properties of base polymers through the introduction of fillers (i.e., microparticles, nanoparticles, fibers, etc.) has historically facilitated replacement of glass, wood and metal with polymer composite counterparts while reducing weight. Various forms of carbon-based nanofillers have been incorporated and commercialized within different polymer matrices; example nanofillers include carbon black, buckminsterfullerene, carbon fiber, carbon nanotubes (CNT), graphene and graphene oxide (GO) or reduced graphene oxide (rGO) derivatives. Within the last decade, graphene and graphene derivatives have received intense focus due in part to the introduction of new methods for producing and manipulating these materials [2-4]. Graphene is a two-dimensional carbonaceous material that exhibits exceptional physical, mechanical, and electrical properties. Typically, it is prepared either by physical exfoliation of high-purity graphite, chemical vapor deposition (CVD) of precursors, or epitaxial growth using SiC crystals [5-10]. Despite the substantial attention focused on graphene nanomaterials in the early 2000s, not many commercialized composites exist today due to the high cost and low purity of the filler. Most of the methods that have been developed to mass-produce graphene nanomaterials often require significant amounts of energy or undesirable reagents during synthesis/processing followed by tedious purification procedures to achieve the most attractive forms [11,12]. In addition, due to the typically poor interactions between the base polymer and graphene, preparing scalable polymer composites with few or no agglomerates still remains a challenge [13].

One highly attractive solution to reduce the cost of preparing carbon-based nanofillers while preserving their excellent properties is to use an oxidized precursor such as GO [14]. GO is commonly prepared using the modified Hummers' method, which combines chemical functionalization with physical exfoliation through vigorous stirring or sonication of cost-effective commercially available graphitic precursors, as illustrated in Fig. 1 [15,16]. During this procedure, structural defects containing oxygen functional groups decorate the surfaces and edges of the individual sheets of graphene. The resulting GO nanosheets are naturally function-

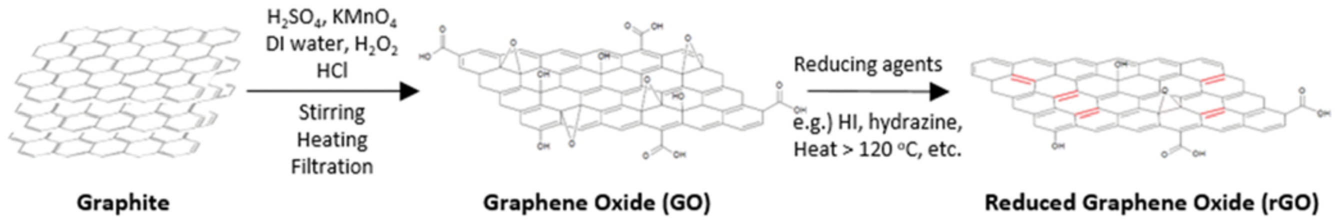

Fig. 1. Scheme of graphite, GO synthesis and reduction to rGO.

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alized with numerous oxidative functional groups, which include hydroxyls, epoxides, and carbonyls, that can be further exploited in other post-processing reactions [15]. Due to the extensive oxidation during the modified Hummers' method, GO is generally insulating and more hydrophilic than graphene [14,17,18]. Yet, it is possible to restore a portion of the electrical conductivity, hydrophobicity and other properties to those approaching pristine graphene by reducing GO to a form called rGO (Fig. 1). This additional step is often implemented using chemical agents [19-27], heat [28-32], or both [33] to carefully tune the chemistry of the GO derivatives. It is noteworthy to point out that many studies have incorrectly stated that rGO is graphene. While rGO is more electrically conductive than GO (has fewer oxidative functional groups on the basal plane), the carrier mobility is substantially lower than pristine graphene because of highly distorted sp^3 bonds left behind after the reduction step [34]. Therefore, we will distinguish rGO and graphene henceforth for clarity.

The carbon-to-oxygen atomic ratio (C/O) for GO and rGO has been reported in literature to be in the range of 1.4 to 40 [35-37]. Among many oxidative functional groups, the majority of epoxide and hydroxyl groups are attached to the basal plane, while a smaller number of carbonyl groups are located primarily at the edge of the sheets. The percentage of epoxide relative to hydroxyl groups may vary depending on the GO preparation procedures and storage conditions. Kim and coworkers reported that GO is metastable even in ambient conditions, and further that the surface chemistry can slowly evolve to reach an increased C/O ratio [38]. Using experimental analysis coupled with density functional theory (DFT), they confirmed that the epoxide group ring opens in the presence of ambient air and enriches the concentration of hydroxyl groups with a relaxation time of ~35 days. The authors claimed that the strained ring-structure of epoxides combined with the presence of C-H bonds in GO favors the disruption of epoxide, resulting in its sequential evolution into hydroxyls. On the other hand, research by Mkhoyan and coworkers confirmed that epoxides are in fact fairly stable, and confirmed the abundance of epoxides over hydroxyls by scanning transmission electron microscope-annular dark field (STEM-ADF) imaging combined with atomic force microscopy (AFM) and DFT calculations [34]. This study concluded that epoxides are more energetically favorable over hydroxyls since the O atom is bonded to two carbon atoms instead of one. And due to the presence of the O atoms, the associated C-C bonds are two-dimensional sp^3 bonds (1.54 Å) rather than sp^2 (1.41 Å, those associated with an ideal sheet of graphene). The randomly distributed O atoms can also create roughness on the sample, which is related to the 0.6 nm average surface roughness detected by AFM scans that can affect packing of multiple layers of GO sheets. It is postulated that these contradicting conclusions from the above two studies could be due to the different sample preparation methods (i.e., oxidation of epitaxially grown graphene sheets from SiC versus direct chemical oxidation of high purity graphite) or detailed storage conditions (i.e., dried in N_2 gas versus vacuum desiccator), etc. Therefore, thoroughly characterizing the surface properties of GO before functionalization and mixing with any polymer or polymer precursor could play a critical role in reproducibility and achieving the targeted structure/properties.

Once the surface functionalities of GO are carefully characterized for the synthesis/processing conditions of interest, Fig. 2 shows representative examples of how polymer composite properties may be tailored by introducing secondary interactions between the polymer or polymer precursor and GO; among many possibilities, these interactions could include hydrogen bonding, π-π interactions and cation-π interactions. Furthermore, covalent bonds can also be implemented by reacting functional groups on the

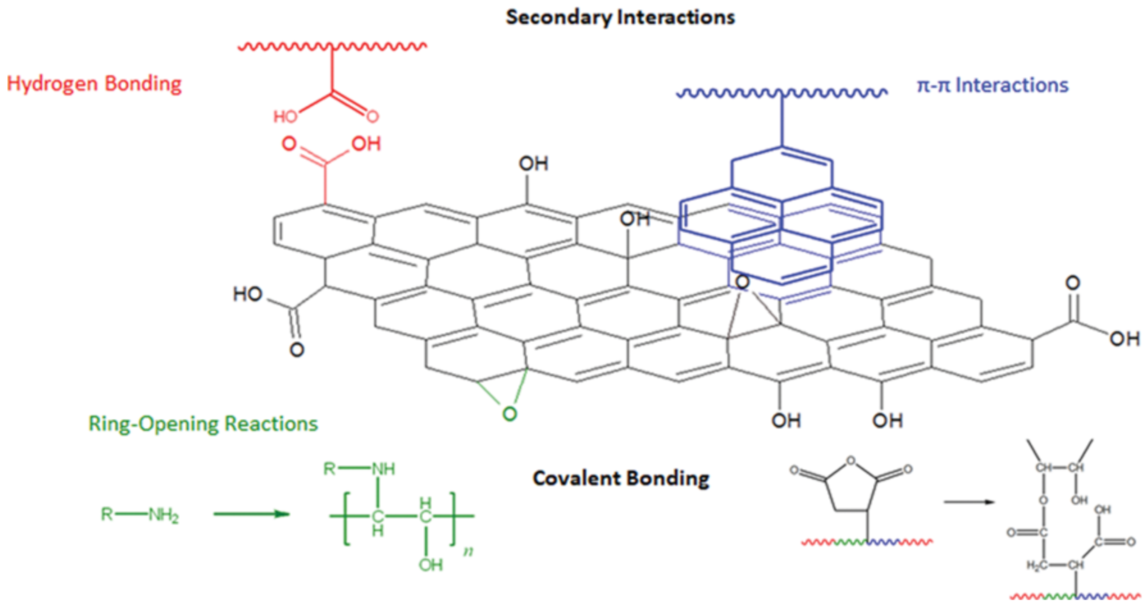

Fig. 2. Summary of possible routes for tailoring functional polymer/GO composites. The top displays representative examples involving secondary interactions. Among many possibilities that could lead to covalent bonds between GO and polymer, the lower two examples display reactions between epoxides on the surface of GO and primary amine or hydroxyls on the surface of GO and succinic anhydride functional groups.

polymer or polymer precursor with the functional groups intrinsically located on GO. These complementary approaches can give rise to a wide range of high performance composite properties spanning rigid epoxy resins to flexible elastomers. The applications these designer materials can serve are equally diverse including advanced sorbents, conductive current collectors for energy storage devices, bendable and stretchable substrates for flexible devices, and composite membranes [39-45].

Among many different types of polymer/GO composites, chemically crosslinked thermosets are indeed an important subset due to the vast array of applications that benefit from both the thermomechanical integrity of a crosslinked material in conjunction with the property enhancements introduced by GO. Therefore, our aim is to provide a background and survey recent research progress related to thermoset GO composites. While there are many ways to prepare composite thermosets, we focus on research that utilizes the GO surface chemistry to form a macromolecular network between the base polymer or polymer precursor and GO nanofiller. These methods include using GO as a multifunctional crosslinker with or without additional chemical modification of the surface functional groups. While inducing chemical reactions between polymer and GO is often straight-forward, it is important to appreciate that the chemical structure and final thermophysical properties can depend strongly on the oxidation state of the GO precursor. Additionally, since GO can be prepared with different atomic C/O ratios, aspect ratios, shapes, and defect densities (i.e., pinhole density, surface roughness, etc.), identifying the surface state of GO with or without additional functionalization is essential for choosing the appropriate polymer or polymer precursor and designing the mixing/post-processing conditions. Therefore, we will begin by briefly surveying analytical methods that are commonly employed to characterize GO and its derivatives.

GO CHARACTERIZATION

Among many characterization methods that are used to study GO composites, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), wide-angle X-ray diffraction (WAXD), and microscopy imaging techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and AFM, are the most widely used. Raman spectroscopy is often employed for characterizing the purity of graphene by comparing the intensities of D (sp^3 carbon atoms originating from structural imperfections created by the oxygen containing groups) and G (sp^2 carbon atoms from the aromatic character) bands. While Raman spectroscopy is clearly valuable for GO research, it often does not provide direct evidence of a chemical reaction between GO and a polymer or polymer precursor due to the Raman-inactivity of typical functionalities of interest; therefore, the other analytical methods listed above will be the point of focus of this review [28].

1. Sample Preparation for Characterization

As mentioned, the specific sample preparation procedure can be important for establishing the surface chemistry of GO; these details can be as important for subsequent characterization as they are for forming the final polymer composite. GO can adsorb a considerable amount of water even in ambient conditions due to the hydrophilic nature of the oxidative functional groups, and this can play a role in defining the surface chemistry. There are several ways to prepare samples, with the simplest way being to prepare a bulk, consolidated film of material by vacuum filtration of suspensions. This process can take a significant amount of time due to the intrinsic clogging of filter pores, and it can lead to restacking or agglomeration of nanoparticles. An alternative method is to vacuum dry in an oven at slightly elevated temperature. While this method can be much faster than filtration, GO could reduce to rGO depending on the temperature, and GO sheets may also restack and agglomerate during drying. A more commonly used method is to lyophilize a solution with a solvent suitable for freeze-drying, typically water for GO. Unlike the other methods mentioned, freeze-drying can minimize restacking of GO sheets while removing water efficiently under vacuum. This simple, scalable and cost-effective method has been also readily used to prepare many polymer composite systems with or without surface modifications [46-48].

2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is one of the easiest and most direct methods for identifying functional groups on the surface of GO. Samples can be either prepared by compressing a KBr pellet containing a fine powder of GO particulates [49,50], coating a thin film of GO on a NaCl or KBr plate, or directly measuring a small amount of GO using the attenuated total reflection (ATR) method [47]. Regardless of the sample preparation method, GO will typically show several distinctive peaks: a broad band of -OH stretching around 3,000-3,700 cm^{-1} (hydroxyl and carboxylic acid groups), C=O stretching at 1,710-1,740 cm^{-1} (carboxylic acid groups), -OH bending at 1,380-1,400 cm^{-1}, C-O stretching at 1,230-1,260 and 1,050-1,070 cm^{-1} (epoxides and hydroxyls), and a strong peak from vibration of water adsorbed on GO superposed with C=C stretching of the graphitic basal plane at 1,620-1,630 cm^{-1} (Fig. 3(a)) [14,32,47,48]. After reducing GO to rGO either by chemical agents or thermal annealing, the intensities of -OH and C-O stretching peaks will diminish substantially, while the C=C stretching peak will increase at around 1,560-1,585 cm^{-1}. The relative degree of reduction from GO to rGO can be confirmed by shifting of the peak location for the C=C absorption peak; this peak will red shift (move to lower wavenumber) as the reduction progresses [14].

FTIR is also a powerful tool for characterizing the surface properties after reacting with a small molecule precursor or polymer. One or more of the oxidative functional groups on GO will decrease in peak intensity, or shift to a different wavenumber depending on the chemistry at play during the reaction. After unreacted precursor or polymer is removed by using an extensive washing procedure, the surface of GO should contain characteristic FTIR peaks of each component with additional signals from the newly formed chemical bonds. Some examples include N-H stretching for primary amines at ~3,400 and ~3,500 cm^{-1} (2 peaks), C-H vibrations at ~2,850 and ~2,920 cm^{-1}, C=O stretching for anhydrides at 1,820 (symmetric) and 1,750 cm^{-1} (asymmetric), C=O stretching for imides at 1,780 (symmetric) and 1,720 cm^{-1} (asymmetric), C=O stretching for esters at 1,730-1,750 cm^{-1}, C=O stretching for secondary amides (Amide I) at 1,630-1,700 cm^{-1}, C=O stretching for urethanes at ~1,650 cm^{-1}, N-H bending for secondary amides

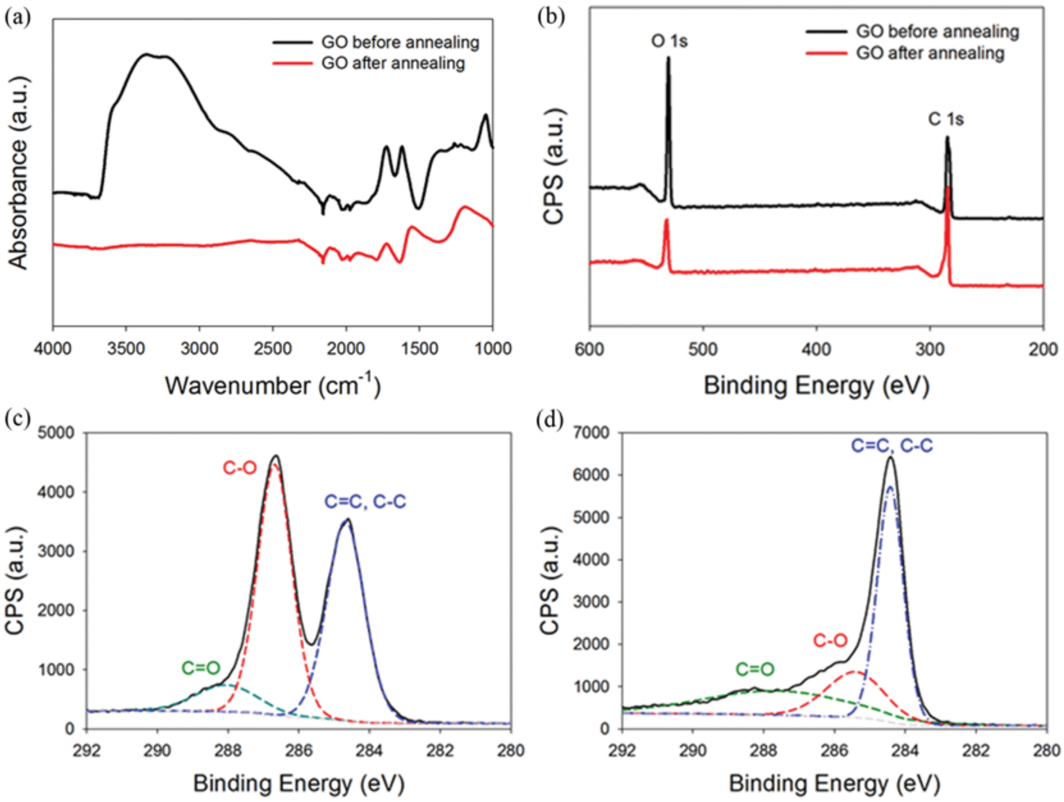

Fig. 3. (a) FTIR spectra before and after thermal annealing of GO. (b) XPS survey and C_{1s} spectra for (c) GO before annealing, and (d) GO after annealing in vacuum at 160 °C for 24 hours. Reprinted with permission from ref. [47]. Copyright 2016 Elsevier.

(Amide II) at ~1,580 cm^{-1} and C-N stretching bonds of amines at 1,020-1,250 cm^{-1}, etc. Note that the newly formed chemical bonds strongly depend on the concentration of the newly formed functional groups, as well as their vibration peak position. Peaks may overlap and superpose with other large peaks, which can make the interpretation difficult as each new bond may not be clearly distinguished. Therefore, other complementary analytical techniques should accompany this characterization in order to develop a complete picture of the reactions that are involved.

3. X-ray Photoelectron Spectroscopy

XPS has been widely adopted for characterizing the oxidative functional groups qualitatively as well as quantitatively. As shown in Fig. 3(b), a typical GO sample prepared using the modified Hummers' method will show two distinctive peaks designated for carbon (C_{1s}) and oxygen (O_{1s}) in a survey spectrum with small impurities depending on the preparation method. The atomic ratio of these two regions is often used to calculated the C/O atomic ratio of a given GO or rGO derivative. The C/O ratio can also be quantified with elemental analysis (EA), which has been reported to show good agreement with XPS [49]. The C_{1s} region of XPS can be deconvoluted into two or more components, where a strong C-C and C=C appear near 284-285 eV and oxygen containing C=O and C-O each appear at 287-289 eV and 286-287 eV, respectively (Fig. 3(c)). Since the concentration of carbonyl groups is relatively lower than epoxide or hydroxyl, the C=O band is usually smaller in area [49]. After GO is reduced by either chemical agents, heat or both, the main oxygen containing components of GO comprising C=O and C-O groups will significantly reduce in intensities/areas, as illustrated in Fig. 3(d). On the other hand, C=C and C-C will become dominant after reduction, as shown by one single peak with a shoulder at higher binding energy. While it is tempting to deconvolute XPS C_{1s} spectra into more than three components, or similarly for the O_{1s} spectra which typically appear as a single broad peak with no shoulders [38], such attempts should be approached with caution. XPS data alone may not provide a persuasive conclusion without additional experimental data to support the deconvolution process and subsequent interpretation.

When XPS data are paired with other complementary chemical analyses, one can also calculate the molar ratio of functional moieties to GO carbon, assuming complete exfoliation. Such an approach can provide a rough estimate of the extent of functionality on the filler material [50]. For example, TGA can be useful for estimating the percentage of reacted functional groups [51]. Typically, the difference in mass loss at the degradation temperature compared to the GO precursor can be attributed to the additional surface modification. However, surface functionalization can be strongly affected by the bulkiness of the attached moieties as well as the GO exfoliation state; it remains challenging to incorporate these factors during such estimations because they are difficult to quantify and therefore introduce uncertainties.

4. Wide-angle X-ray Diffraction

WAXD is commonly employed to identify the interlayer spacings between graphene derivative sheets, i.e., to determine how well the sheets are exfoliated into single or a few layers of sheets.

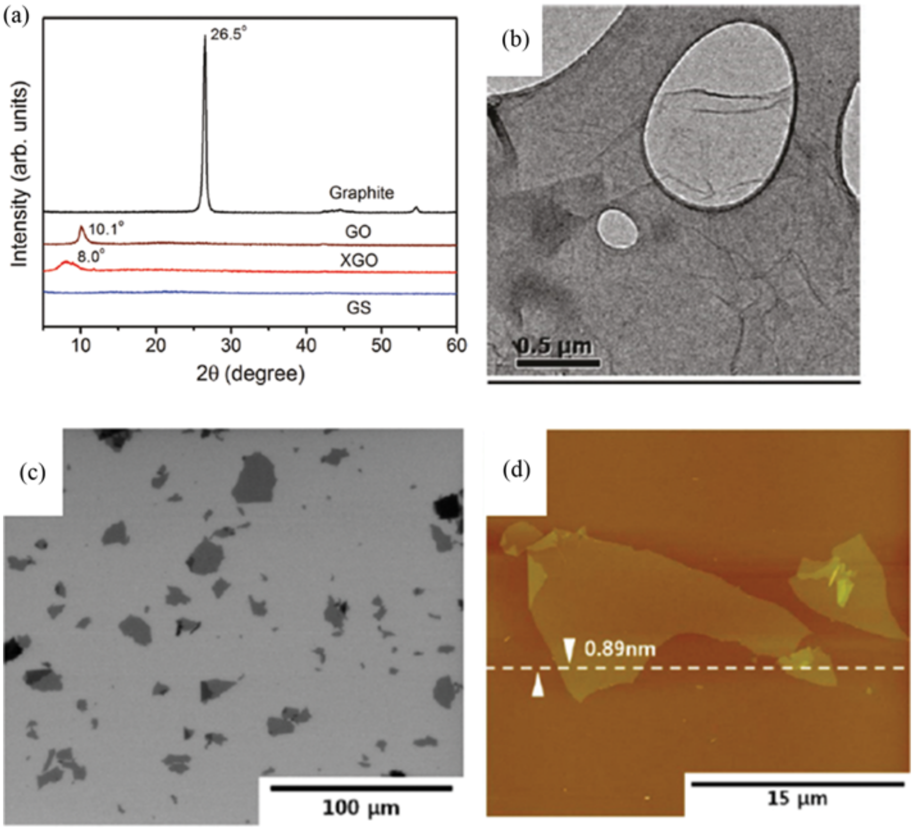

Fig. 4. (a) WAXD measurements for graphite, GO, exfoliated GO by the intercalation of water molecules (XGO), and completely exfoliated graphene sheets (GS). (b) TEM image of graphene sheet on a Lacy-carbon grid. Modified and reprinted with permission from ref. [49]. Copyright 2011 American Chemical Society. (c) SEM image of GO sheets and (d) AFM image of a single GO sheet with thickness variation indicated along the dotted line between the arrows. Reprinted from Open Access article ref. [31].

For graphite (the common precursor for preparing GO), the Bragg angle 2θ appears ca. 26° with a narrow sharp peak, which corresponds to a *d*-spacing of 0.34-0.36 nm between atomic planes. On the other hand, GO may show a broad low intensity peak at the Bragg angle of ~10° (*d*-spacing of 0.74-0.94 nm) depending on the degree of chemical/physical exfoliation resulting from the modified Hummers' method and the amount of adsorbed water. Completely exfoliated or single layers of graphene derivative sheets will show no peak, as shown in Fig. 4(a).

After the surface of graphene derivatives is modified with small molecule precursors or polymers, the *d*-spacing will increase depending on the size, shape, and rigidity of the newly attached compound. If a catalyst, reducing agent, or heat is applied during the surface modification step, the resulting GO derivative may undergo reduction and form rGO. A more obvious observation of this reduction is the color change from light brown to black after surface treatment. An important goal for improving the physical properties of polymer/GO composites at low content of GO fillers is to increase the interlayer *d*-spacing as much as possible, often by reducing the interlayer attraction or affinity of the matrix for the nanofiller surface.

5. Microscopy Imaging

While understanding the surface functionality of GO is important for designing chemical reactions between polymer and GO, the size, shape, and thickness of GO nanofillers will influence a number physical properties and final performance of the composite in targeted applications. A simple and practical method to identify the size and shape of GO is to conduct SEM or TEM imaging, where an example is shown in Fig. 4(b)-(c). Due to the distorted sp^3 bonds originating partly from the numerous oxidative functional groups, GO sheets are typically wrinkled or crumpled in shape and are often stacked as a few layers of sheets. By examining a low magnification SEM image of GO particles distributed on a substrate as shown in Fig. 4(c), it is straightforward to measure the lateral dimension and size distribution of multiple GO platelets. The lateral dimension is typically in the range of a few hundreds of nanometers to tens of micrometers.

Meanwhile, instruments utilizing proximal nanoprobes, such as AFM, are suitable for measuring the average thickness of the exfoliated GO platelets. According to AFM studies (an example is shown in Fig. 4(d)), the thickness of a single layer of a graphene derivative sheet may range from 0.6-1.2 nm. Theoretically, graphene sheets with van der Waals thickness have been reported to be ca. 0.4 nm [5].

POLYMER/GO COMPOSITES USING GO WITHOUT FUNCTIONALIZATION

While a prevalent strategy for forming polymer/GO compos-

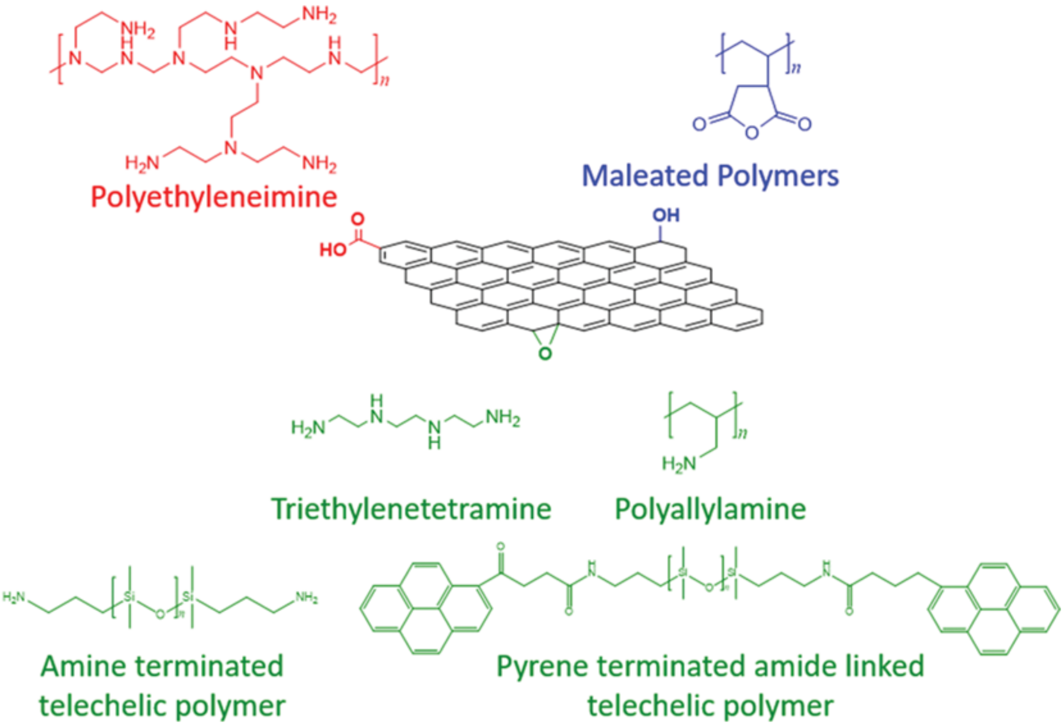

Fig. 5. Summary of possible polymers and polymer precursors that may be used to synthesize functional polymer/GO composites using GO as a multifunctional crosslinker.

ites has been physically blending or compounding polymer and GO using heat or solvent, several recent studies have focused on developing new composite materials by forming covalent bonds between the polymer and intrinsic functional groups on GO (i.e., no additional functionalization or pretreatment of the GO is performed). The formation of covalent bonds between the many oxidative functional groups naturally located on the surface of GO and functional polymer precursors has resulted in the high throughput production of mechanically robust thermosets. In these often two-component systems, GO serves as both a mechanical reinforcing agent and multifunctional crosslinker. The final properties (tensile modulus, elasticity, hand-feel, etc.) of the thermosets can be tailored by modifying the polymer precursor structure and functionality. In addition, the crosslinked molecular network within these composites redefines their upper service temperature to be commensurate with that of breaking covalent bonds instead of intrinsic thermal transitions (e.g., glass transition or crystal melting temperature) and, although they will solvent-swell, they are generally solvent insoluble. If processed appropriately, a composite with a highly dispersed filler can result that is attractive for many practical applications. Combined with the cost-effective pathway to synthesize GO, this chemistry-centric composite design strategy has introduced new opportunities for research and commercialization of GO-based composites.

The following examples suggest that this technology is compatible with virtually any polymer system provided that proper chemical functionalities are implemented and the interplay of crosslinking reaction kinetics, rheology and processing conditions is carefully managed. It is clear that future fundamental research merging simultaneous reaction and processing of GO based composites could greatly expand the potential of these materials.

1. Reaction with Hydroxyl Groups

A recent report on accessing hydroxyl groups of GO as a crosslinking site was described by Shi et al. [52]. For this study, SEBS-g-MA (styrene-ethylene-butylene-styrene block copolymer grafted with maleic anhydride, primarily attached to butylene units) was solution mixed with GO (GO was pretreated with an amine surfactant in order to prevent agglomeration of particles during solution mixing) in order to improve the electrical and mechanical properties of the composite as shown in Fig. 5. They proposed that an esterification reaction occurred between the anhydride groups on the polymer and hydroxyl groups on GO by comparing a series of FTIR spectra. However, FTIR data in this study shows residual C=O stretching peaks from anhydrides that could suggest the reaction was not complete; this is consistent with the fact that the mechanical properties of the composite were not improved significantly. SEBS-g-MA composites with 4 wt% GO showed a moderate increase in tensile strength and modulus (average of 55% increase), while the elasticity deteriorated by half. Generally, this approach is attractive because commercial maleated polymers have been used for many years as compatibilizers for polymer composites or for promoting adhesion between dissimilar layered film materials. Considering the impact of maleated polymers and the possibility of forming chemical crosslinks without additional functionalization of GO filler, further research on this topic will be important in the future.

2. Reaction with Epoxide Groups

Utilizing epoxy groups on the surface of GO to perform reactions with polymer or polymer precursors requires extra precaution because epoxy reactions are generally sensitive to the presence of water, which could potentially affect the curing kinetics as well as the glass transition temperature of the final composite (i.e., depending on the degree of crosslinking) when water content is higher than 1% [53]. Due to the hydrophilic nature of GO, a considerable amount of water can be adsorbed on the surface when it is exposed to ambient air. The amount of water adsorbed to the surface of GO can be easily determined by conducting a TGA experiment [54], and, likewise, can be removed effectively upon heating. However, thermal heating can also promote reduction of GO to rGO and unintentionally sacrifice the oxidative functional groups that are targeted for introducing covalent bonds with the polymer. To prevent such effects, GO should be fully dried in a high vacuum oven at a low temperature for a long period of time and used immediately if possible. Otherwise, dried samples should be kept in a desiccator equipped with a humidity sensor to ensure high yielding reactions with the polymer's functional groups.

The first relevant study of chemical crosslinking reactions using epoxide groups of GO was by Park and coworkers who synthesized polyallylamine/GO composite paper (chemical structure in Fig. 5) [55]. They performed an epoxy-amine reaction in an aqueous colloidal suspension by sonicating the mixture for 6 hours. No heat or additional catalysts were used other than the prolonged sonication procedure. The occurrence of the chemical crosslinking reaction was supported by FTIR and XPS spectra, where a significant reduction in C-O (epoxy) was observed. One may hypothesize that the decrease in the epoxide group could be partially due to the extensive sonication driving reduction of GO; this appears consistent with the fact that polyallylamine modified GO sonicated solutions were darker in color than the neat GO solutions at the same concentration (i.e., because of partially reduced GO due to sonication). In addition, a new peak for C-N appeared seemingly consistent with an epoxy-polyallylamine reaction, although it is unclear how this signal was deconvoluted from that intrinsically associated with polyallylamine alone. The tensile strength of the final composite paper showed a moderate ~10% enhancement and the tensile modulus increased by 95% with the addition of polyallylamine. This short communication was one of the first reports to highlight GO as a potential chemical crosslinker for synthesizing composite thermosets via epoxy-amine reactions with polymers.

Later, a similar epoxy-amine reaction was implemented by a different research group for synthesizing a highly flexible epoxy/GO aerogel [56]. A solution of 1,4-butanediol diglycidyl ether (BDGE) and triethylenetetramine (TETA, chemical structure in Fig. 5) was mixed with a certain amount of GO in water and then freeze-dried to obtain a highly elastic thermoset composite aerogel. Epoxy resin was incorporated within the GO aerogel skeleton to form covalent bonds between the amine groups of TETA and epoxide groups on the surface of GO. The final composite was high in compressive strength (230 kPa), low in density (90 mg/cm^3), but exhibited high elasticity as the material could recover its original volume when compressed up to 50% without substantial irreversible deformation.

Inspired by this prior work, the Ellison group also reported a simple and straightforward method to form a chemically crosslinked GO composite elastomer by forming a macromolecular network between poly(dimethylsiloxane) (PDMS) and GO [47,57]. Ha and coworkers demonstrated that primary amine functional groups on

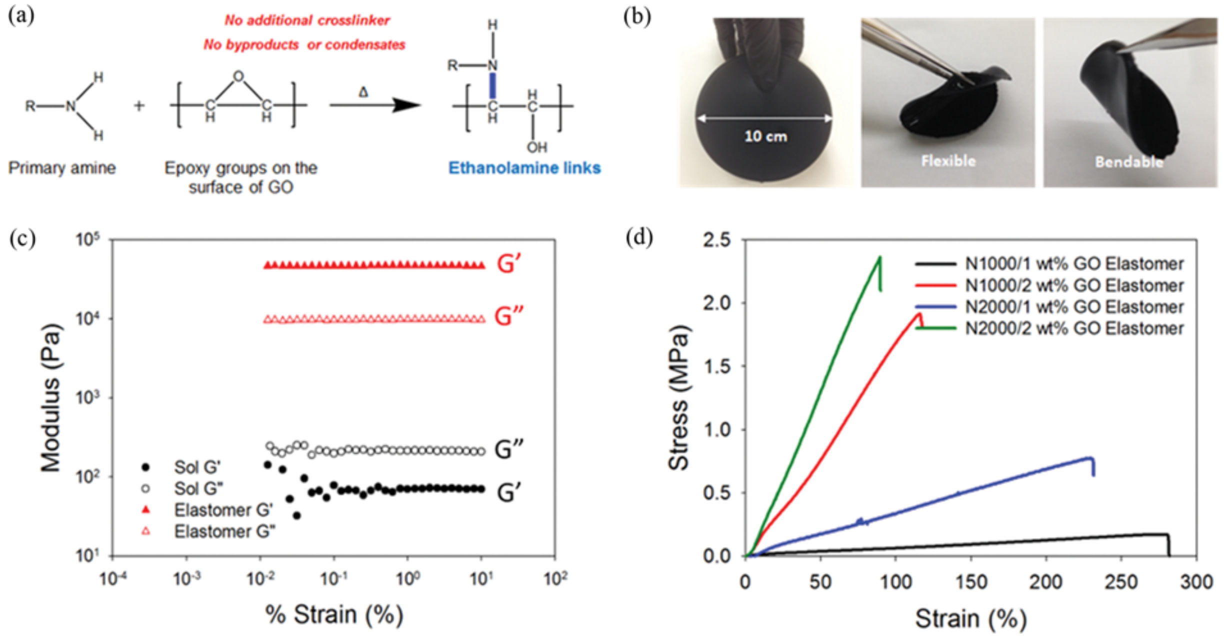

Fig. 6. (a) Primary amine terminated telechelic polymer forms robust covalent bonds when reacted with epoxy-containing multifunctional crosslinker GO. No additional crosslinkers or catalysts are required and no byproducts or condensates are generated during the reaction. (b) This method is scalable and the crosslinked elastomers are flexible and bendable. (c) Rheological property comparison before and after the curing reaction. (d) By simply modulating the concentration ratio of polymer and GO precursors, various physical properties can be tailored with ease, here shown in the context of a stress-strain tensile experiment. Modified and reprinted with permission from ref. [47]. Copyright 2016 Elsevier.

the end of telechelic PDMS oligomers can undergo crosslinking reactions with epoxies on GO during simple heating (Fig. 6(a)). In this system, as shown in Fig. 6(b), a liquid polymer precursor transforms into a solid elastomer by incorporating as low as 0.44 volume% of GO filler and heating. The presence of covalent bonds is supported by FTIR, swell ratio, gel content, as well as mechanical and rheological property measurements (Fig. 6(c)-(d)). The GO not only acts as a filler material which reinforces various properties, but also participates as a multifunctional crosslinker, thereby promoting elastic properties. For example, the elastomers prepared in this work contained more than 75% insoluble gel and were capable of extending up to 300% of their original length [47]. Since the reaction is controlled by the concentration of epoxy and amine functional groups, crosslink densities and other physical properties were simply tuned by controlling the concentration of polymer (multifunctional amine) and GO (multifunctional epoxy). This scalable material design strategy starting from two low-cost materials, graphite and polymer, could enable more versatile usage of polymer/GO elastomers in a number of practical applications. One notable example demonstrated by the Ellison and Freeman groups was its use as a CO_2 gas separation membrane, where the composite membrane was able to achieve gas permeability and selectivity combinations comparable to many high performance polymers, such as polyimides [57].

Recently, the above mentioned epoxy-primary amine mechanism was investigated in model reactions between GO and polyethylene glycol monomethyl ether amine [58]. While there is literature proposing that an amidation reaction can occur between primary amines on polymers and carboxylic acids located at the edge of GO [59,60], Vacchi et al. concluded that a more prevalent reaction occurs by ring-opening of the epoxides on GO, which was supported by solid state NMR, XPS, and FTIR analyses. In a similar line of research, Acocella et al. suggested that GO can act as a catalyst for epoxy resin curing systems [61]. By curing bisphenol-A diglycidyl ether (diepoxy) with a diamine crosslinker, they observed that the addition of GO reduced the gel time as well as the gel temperature. Considering a number of previous studies including that by Vacchi et al., it is more likely that GO participated in the curing reaction by providing alternative epoxy ring-opening sites, instead of as a catalyst.

More recently, the Ellison group also demonstrated that secondary amide groups are capable of undergoing epoxy ring-opening reactions. Although the stable resonance structure of a secondary amide functional group means its reactivity is usually lower than primary amines, it can be accelerated by introducing a catalytic functional group that can facilitate the reaction through molecular templating [62]. Considering the vast array of materials containing secondary amides, such as amino acids, DNA, and nylons, polymer/GO composite systems formed by epoxy-secondary amide reactions are highly practically relevant. Ha and coworkers showed that a catalytic functional group (here a pyrene group) can simply assist in bringing the secondary amide group in close proximity with the GO surface to greatly enhance the efficacy of the epoxy-secondary amide reaction. From another viewpoint, the action of

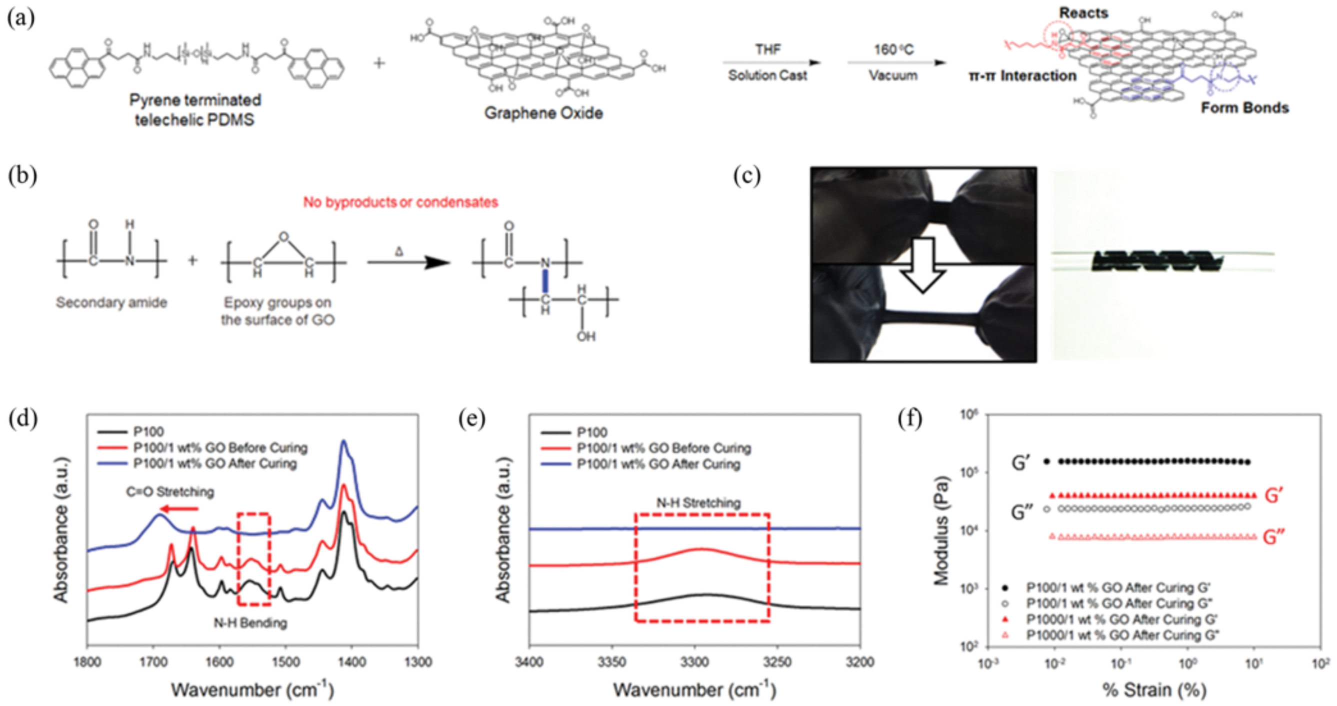

Fig. 7. (a) Synthesis of molecularly templated PDMS/GO elastomer. (b) The reaction takes place between secondary amide and epoxide to form covalent crosslinks. No byproducts or condensates are generated during the reaction. (c) After the crosslinking reaction occurs, the elastomer is flexible and stretchable. (d) FTIR spectra for the region from 1,300 to 1,800 cm^{-1} and (e) 3,200 to 3,400 cm^{-1} confirming the reaction shown in (b). (f) Rheological property comparison with different molecular weights of PDMS (i.e., different concentration of secondary amide groups) after the curing reaction. Modified and reprinted with permission from ref. [62]. Copyright 2017 Wiley.

the pyrene catalyst enhances the local concentration of the secondary amide groups near the surface of GO compared to that of bulk. A schematic illustrating this reaction is shown in Fig. 7(a)-(b). As a result, depending on the overall concentration of amide and epoxy groups in the system, the resulting polymer/GO composite elastomers were highly crosslinked (i.e., up to 96% insoluble gel) and at the same time highly elastic in that they could be stretched up to 200% of their original length (Fig. 7(c)). This finding was supported by FTIR (Fig. 7(d)-(e)), mechanical and rheological properties (Fig. 7(f)) as well as compared with the same polymer lacking a catalytic functional group (i.e., an appropriate control sample), to prove the concept of the molecular templating reaction.

In summary, extensive research utilizing the surface epoxide group of GO to form polymer thermosets has been reported that points towards the significance of understanding and leveraging reactive epoxide functional groups on the surface of GO for amine and amide containing curing systems. It is clear that future research will only further expand the palette of reactions that will exploit epoxides on GO driving towards advanced thermoset materials.

3. Reaction with Carboxylic Acid Groups

Studies of chemical crosslinking reactions utilizing carboxylic acid groups (mostly located on the edge of GO) have not been as prevalent as those that exploit epoxy groups on GO. One possible explanation could be the simplicity and efficacy of the preferential reaction of primary amine with epoxide compared to carboxylic acid groups [58], even in the absence of catalysts or coupling agents in the system. Even so, there are a few studies that suggest an amidization reaction occurs when amines and carboxylic acids are charged in basic aqueous solution. Zhou et al. and Sui et al. both used polyethyleneimine (PEI) to react with GO in an alkali solution with moderate heat to form amide linkages and a crosslinked material [63,64]. Zhou and colleagues first decorated the surface of GO with PEI to use it as a catalyst to deposit Fe-Ni nanoparticles for the dehydration of ammonia borane [63]. They confirmed the presence of newly formed amide groups using FTIR and XPS, where the C=O stretching vibration of the carboxylic acid ($1,730\ \mathrm{cm}^{-1}$) disappeared and a strong C=O band at $1,624\ \mathrm{cm}^{-1}$ appeared after mixing, which was assigned to amide I bonds. The N_{1s} spectrum of the PEI/GO composite was deconvoluted into three subpeaks at 399, 400 and 402 eV which were assigned to amide, amine (C-NH and C-NH_2) and N^+ species, respectively. Both of these analytical results were consistent with the formation of new amide bonds between PEI and GO. Similar to Zhou's work, Sui and coworkers prepared PEI/GO composite aerogels for colorant/dye and gas adsorption applications [64]. For these applications, the abundant amino groups from the PEI component promoted good adsorption of acidic gas or anionic materials, which motivated their work to synthesize a highly porous aerogel adsorbent. The analysis method and interpretation identifying the formation of amide groups was identical to Zhou's research, confirming that PEI chemically crosslinked with the surface of GO. However, both of the studies used PEI as a simple additive to decorate the surface of GO for a particular application, and in the absence of data related to the crosslink density, swell ratio, or gel content of the macroscopic material, it is difficult to conclude whether PEI/GO materials truly formed a thermoset with a broader macromolecular network rather than being composed of crosslinked subunits held together by van der Waals forces or physical entanglements. Nonetheless, these studies revealed the possibility of forming secondary amide groups utilizing carboxylic acid functional groups on GO and amino groups on the polymer which will surely expand in scope in the future.

POLYMER/FUNCTIONALIZED GO COMPOSITES

There are several advantages to functionalizing the surface of GO with different chemical moieties over using pristine GO. First, the diversity of functional groups that can form chemical bonds (i.e., crosslinks) or other interactions can be greatly expanded over those available via unmodified GO. Second, these additional functionalities can be exploited and tuned over a wide range to improve the compatibility and miscibility between the filler and polymer matrix. Methodologies to modify the surface of GO generally bind functional compounds to the GO by formation of covalent bonds or non-covalent interactions, such as hydrogen bonding, coordination bonding, and π-π interactions. A recent review on the synthesis and properties of polymer/functionalized GO composites emphasized the significance of surface modification in detail [65]. In some cases, it has been demonstrated that functionalized GO can outperform pristine graphene and GO even at lower total concentration of nanofiller in the composite, although it is anticipated that this could be system and/or processing method dependent [46]. This section of the review will focus on recent research employing functionalization methods for forming GO-based composite thermosets that display significant improvements in mechanical properties.

1. Functionalizing GO with Silanes

While modifying the surface of GO with different functionalities can be fairly straightforward in many cases, appropriate modification and sample preparation is required to ensure suitable crosslinking occurs to later form a thermoset. Otherwise, surface modified GO will simply contribute as a compatibilizer or more typical physically dispersed nanofiller. Such a result was observed by Zhang and coworkers, where the surface of GO was functionalized with 3-aminopropyltriethoxysilane (APTES), and mixed with a hydroxyl terminated PDMS precursor, as illustrated in Fig. 8(a) [51]. By comparing the thermoset composite with and without chemical crosslinker tetraethyl orthosilicate (TEOS), they concluded that the APTES-GO did not participate in the crosslinking reaction and the modest modulus enhancement was solely due to physical reinforcement. It is hypothesized that the crosslinking reaction did not occur due to 1) the hydrolysis of triethoxysilanes on the surface of GO while exposed to air, 2) self-condensation reactions during GO modification in the presence of the basic secondary amide linkage, or 3) reaction of triethoxysilane functional groups inter- or intramolecularly with other hydroxyl groups on the surface of GO. Interestingly, the aspect ratio of the modified GO filler also decreased from 1,500 for pristine APTES-GO to 62 after incorporating into the PDMS thermoset, perhaps supporting explanation 3) which would be expected to form GO aggregates.

In another study, Xie and coworkers functionalized the surface of GO with a sulfide containing silane coupling agent [Bis(trietho-

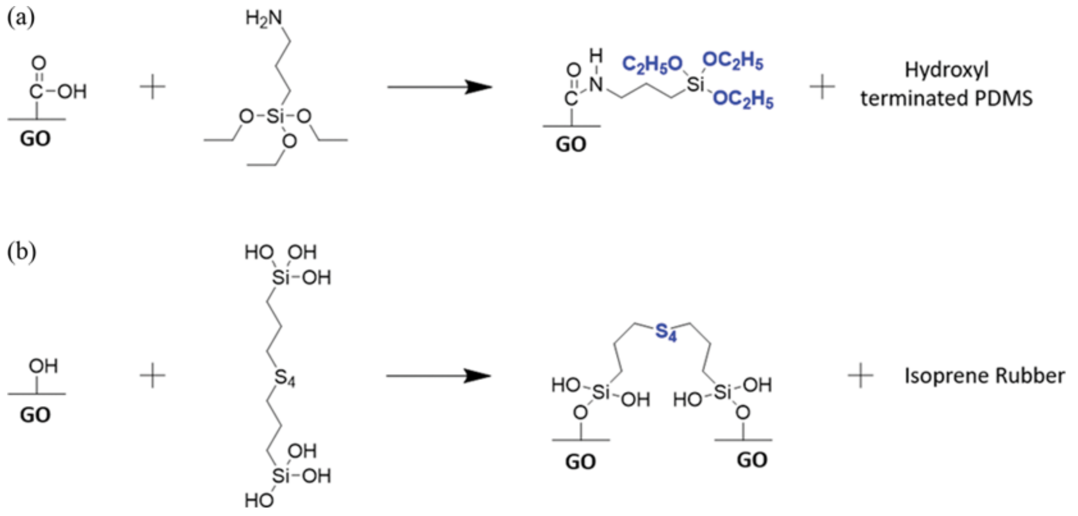

Fig. 8. **(a) Functionalizing the surface of GO with APTES by forming a secondary amide linkage. Ethoxy groups can react with hydroxyl end groups on the polymer to form crosslinks. (b) Functionalizing the surface of GO with BTESPT by forming Si-O bonds. Sulfides can vulcanize polyisoprene rubber and form chemical crosslinks. Reactive functional groups participating in the crosslinking reaction are in bold and color.**

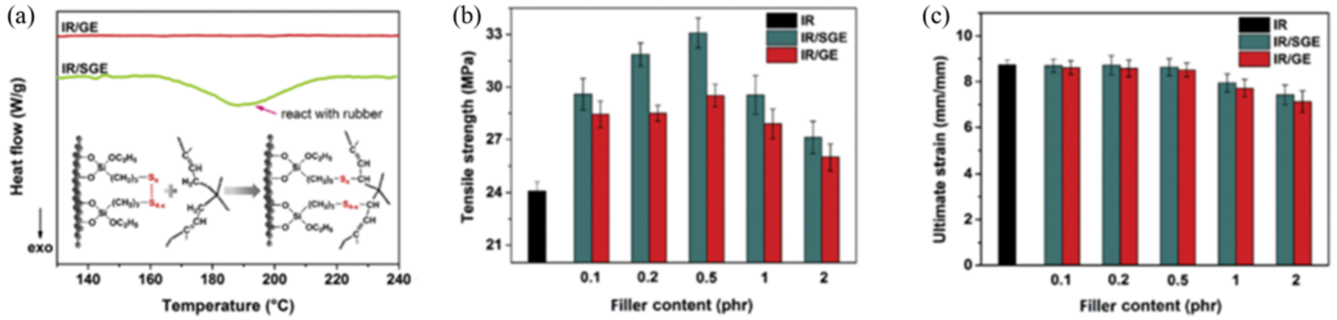

Fig. 9. **(a) DSC scan of polyisoprene rubber with GO (designated GE in the original figure) and surface modified BTESPT-GO (designated SGE in the original figure). No additional curing agent was used and the total filler loading was five parts per hundred. BTESTP-GO undergoes crosslinking with the polyisoprene upon heating which generates an exothermic reaction peak. Comparison of (b) tensile strength and (c) ultimate strain of polyisoprene rubber composites at different filler loadings. Modified and reprinted with permission from ref. [66]. Copyright 2017 Elsevier.**

xysilylpropyl)tetrasulfide, BTESPT] and successfully formed chemical crosslinks with polyisoprene rubber as shown in Fig. 8(b) [66]. Like vulcanization of an ordinary rubber tire, polyisoprene rubber reacted with the sulfide groups bonded to the surface of GO as confirmed by FTIR and DSC studies (see Fig. 9(a)). The authors found that the "bound rubber layer" was thicker for BTESPT-GO nanofiller than unmodified GO, suggesting the influence of the local crosslinking reactions and/or the existence of stronger interfacial interactions for the BTESPT-GO nanofiller. As summarized in Fig. 9(b)-(c), a more efficient load transfer occurred during uniaxial deformation. By incorporating only 0.5 parts per hundred of BTESPT-GO, tensile strength was improved by 37% while the elasticity of the rubber remained unchanged. Both properties showed a steady decrease at higher filler concentrations, and the authors hypothesized that this behavior was due to filler agglomeration as confirmed by TEM. This result successfully demonstrates that silane coupling agents can be an important tool for decorating the surface of GO for later crosslinking reactions.

2. Functionalizing GO with Amines

As described in the previous sections, epoxy-amine reactions have been readily implemented in many polymer/GO composite studies. Instead of reacting epoxide groups of GO with amines on the polymer, one can also design an epoxy-amine system by functionalizing the surface of GO with amines and then reacting with the epoxy resins. Some examples of such reactions are illustrated in Fig. 10. Park and colleagues prepared amine-terminated poly(butadiene-*co*-acrylonitrile) (ATBN) modified GO to toughen epoxy resins at a GO loading less than 0.1 wt% (Fig. 10(a)) [46]. To prepare amine functionalized GO crosslinkers, 4,4′-methylene diphenyl diisocyanate (MDI) was used as a coupling agent, and the surface modification was confirmed using FTIR, TGA, and WAXD. While many studies use solvents and dispersions with relatively high concentration of filler, Park and coworkers directly incorporated ATBN-GO into a low viscosity amine-functional crosslinking agent (Jeffamine® D230) and ultrasonicated using a probe sonicator to obtain an optimal dispersion. After mixing with an epoxy resin and cur-

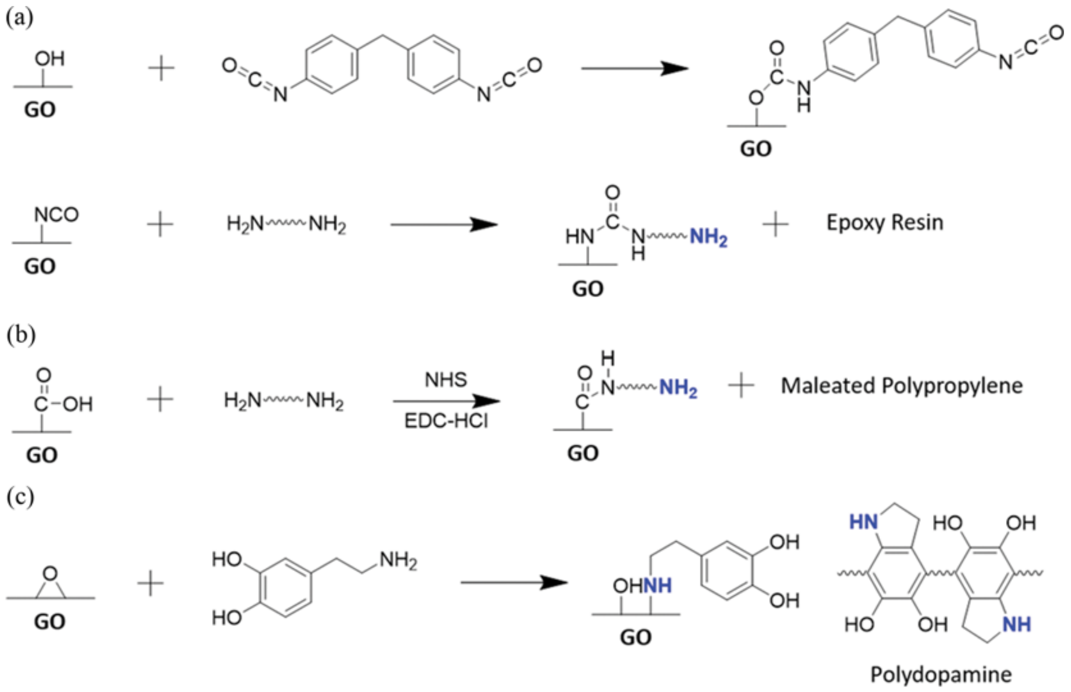

Fig. 10. (a) Functionalizing the surface of GO with MDI followed by amine terminated telechelic polymer. Primary amine groups can react with epoxide groups of an epoxy resin to form crosslinks. (b) Functionalizing the surface of GO with amine terminated telechelic polymer by forming an amide linkage. In this case, primary amine groups reacted with maleated polypropylene in order to form chemical crosslinks. (c) Functionalizing the surface of GO with dopamine and polydopamine in order to form secondary amine groups for further reaction with an epoxy resin. The reactive functional groups participating in the crosslinking reaction are in bold and color.

ing, they observed a 50% increase in fracture toughness and 140% improvement in fracture energy with respect to the neat epoxy resin by incorporating 0.04 wt% surface modified GO. They concluded that these results were attributed to the good dispersion of filler accompanied with the inclusion of the elastic rubber component (i.e., poly(butadiene-*co*-acrylonitrile)) as well as the introduction of covalently bonded filler-matrix interfaces. Since the concentration of the surface-treated GO was extremely low, it is somewhat unclear how much crosslinking can be attributed to the GO filler versus the amine-functional crosslinked agent.

Song et al. modified the surface of GO with primary amines by reacting GO with amine functionalized telechelic poly(ethylene glycol) (Fig. 10(b)) [67]. A combination of N-hydroxysuccinimide (NHS) and carbodiimide coupling agents (EDC-HCl) was used to improve the reaction between the carboxylic acid groups of the GO and primary amines of the polymer. Then, the surface modified GO was solution blended with maleated polypropylene to form amide crosslinks by the ring-opening reaction of succinic anhydride functional groups. Although no significant improvements were observed in mechanical properties, notable enhancements in flame retardant properties were shown with 2 wt% filler materials. The total heat release (THR) and peak heat release rate (PHRR) declined by 44% and 39%, respectively, which are two important quantities that characterize the flammability of materials in a fire.

Mussel-inspired dopamine has been also used as a surface modifier for GO due to its universal adhesive ability that can impart good dispersion and strong interfacial adhesion when applied in polymer composites. During the oxidative polymerization of dopamine in a weak alkaline condition, newly generated electrons and protons can effectively reduce the oxidative functional groups on the surface of GO, while physically adhering to the graphene basal plane by secondary interactions [59,68]. In addition, the primary amine of the dopamine monomer can also react with the epoxide on the surface of GO, and provide secondary amines and hydroxyl groups through ring-opening reactions. This strategy can prevent agglomeration of GO sheets as well as enhance the interfacial adhesion between the filler and polymer matrix. Although a number of studies claim that secondary amides can also form via primary amines of dopamine monomer reacting with carboxylic acids of GO, it is unlikely such a reaction will occur at room temperature without any catalysts or heat. Nonetheless, secondary amine linkages can undergo reactions with epoxy resins at high temperature with/without catalysts, which has been demonstrated by Hu et al., and Li et al. [59,60]. Both of these studies functionalized the surface of GO with polydopamine (PDA) and mixed the product with epoxy resin to form a crosslinked thermoset composite, as illustrated in Fig. 10(c). While Hu and coworkers focused on thermal and mechanical properties, Li investigated the curing kinetics in depth by comparing the activation energy of a system with/without PDA-GO (see also Fig. 11). As a result, both studies concluded that the secondary amine formed between PDA and GO can undergo epoxy ring-opening reactions with the base matrix (Diglycidyl ether bisphenol A, DGEBA) when cured at high temperature. The exothermic temperature for the composite shifted ca. 1 °C, suggest-

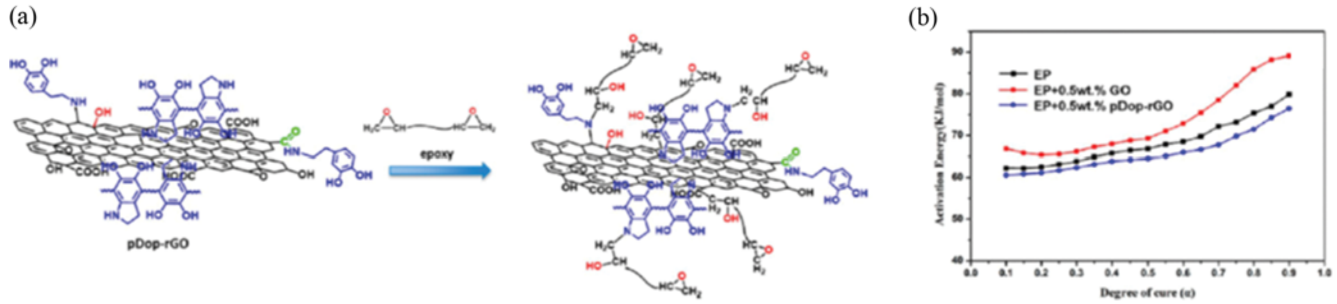

Fig. 11. (a) Proposed reaction scheme for PDA-GO with epoxy resin. (b) The variation of the activation energy with respect to the degree of cure. The epoxy composite with PDA-GO (in graph, pDop-rGO) shows the lowest activation energy, indicating that PDA-GO participated as an additional crosslinker. Modified and reprinted with permission from ref. [60]. Copyright 2017 American Chemical Society.

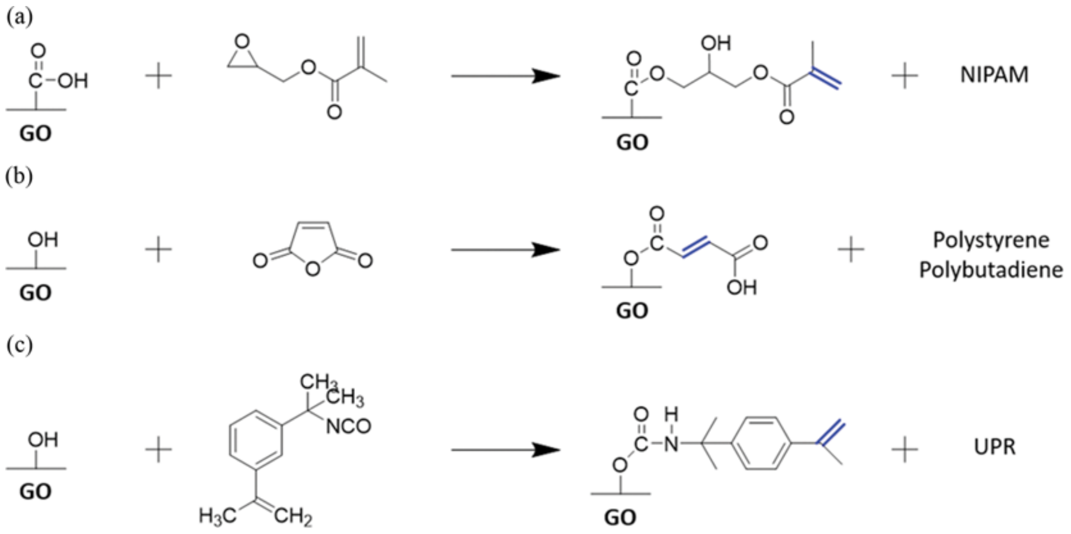

Fig. 12. (a) Functionalizing the surface of GO with glycidyl methacrylate. A crosslinked hydrogel can be synthesized by reacting the product with NIPAM monomer in aqueous solution. (b) Functionalizing the surface of GO with MA to form additional ene functional groups. Surface modified GO with the new ene functionality acts as a grafting site for *in situ* polymerization. (c) Functionalizing the surface of GO with TMI by forming a urethane linkage. Unsaturated polyester resin can react with the ene functional group to crosslink and toughen the composite. The reactive functional groups participating in the crosslinking reaction are in bold and color.

ing that PDA-GO acts as a catalyst to accelerate the curing reaction. Furthermore, the enthalpy of reaction increased substantially with less than 1 wt% PDA-GO, confirming the presence of additional chemical crosslinking reaction sites due to the modified filler addition. Li also confirmed that the activation energy for the crosslinking reaction was slightly reduced by ~4%. Note that the occurrence of crosslinking reactions was derived from FTIR and XPS peak deconvolutions. As mentioned, the deconvolution process should be interpreted with caution. Since PDA intrinsically contains C-N bonds within the chemical structure, it can be difficult to determine whether the C-N bond is due to the PDA polymer or the reaction with the bulk epoxy. Nonetheless, comparing the physical and thermochemical properties (i.e., curing kinetics) of the composites with and without PDA functionalization supports the fact that this is a viable and attractive strategy.

3. Functionalizing GO with Ene

Another important functionalization is to modify the surface of GO with moieties containing C=C or "ene". Ene modified GO can polymerize with monomers that undergo addition polymerization by the "grafting to" or "grafting from" method forming a thermoset even at low concentration of filler materials. Lo and coworkers reacted carboxylic acids on the surface of GO with glycidyl methacrylate by an esterification reaction (Fig. 12(a)). N-isopropylacrylamide (NIPAM) monomer with additional crosslinkers was then added to the mixture and photopolymerized in order to form a 3-D network hydrogel [69]. Due to the stimuli-responsive characteristic of the polymer matrix, the resulting composite hydrogel exhibited a strong response to IR irradiation which could be potentially useful in light activated actuators and microfluidic devices.

Anhydride can also provide additional C=C functional groups when grafted on the surface of GO (Fig. 12(b)) [70-72]. These studies have demonstrated that MA can easily react with hydroxyl groups on the surface of GO at elevated temperatures. The additional C=C bonds generated after ring-opening MA can promote *in situ* polymerization with various monomers to form crosslinked polymers of polystyrene and polybutadiene. All of the reports showed substantial enhancement in a number of mechanical properties by incorporating GO nanofiller and improving interfacial interactions between the polymer matrix and nanofiller.

He et al. proposed a method to crosslink unsaturated polyester resins (UPR) with surface modified GO (Fig. 12(c)) [50]. For this study, both 3-isopropenyl-α,α-dimethylbenzylisocyanate (TMI) and dodecylamine (DDA) modified GO fillers were synthesized. TMI-GO was capable of covalent bonding with UPR, while the DDA improved the surface compatibility with the polymer matrix. The dispersion of the composite was confirmed using TEM analysis and, as expected, TMI-DDA-GO showed the best dispersion. In terms of mechanical properties, 0.04 wt% of TMI-DDA-GO showed the best toughening results, where a 55% increase in fracture energy was obtained with little or no change in other mechanical properties. Interestingly, in comparing different processing methods (in this case, mechanically stirred and ultra-probe sonicated), the non-sonicated TMI-DDA-GO containing composites showed an even greater toughening effect. The authors proposed that while sonication can improve dispersion of the filler, fillers may decrease in size due to attrition during sonication; here, a decrease in average filler size is detrimental to the toughening mechanism.

4. Other Methods to Functionalize GO

Beside the core topics mentioned above, many other chemical reactions can be employed to modify the surface of GO as summarized in Fig. 13. Similar to the studies of Park et al. [46], Li and coworkers prepared an MDI modified GO and *in situ* polymerized with step-growth monomers to form poly(ether imide) composite thermosets [73]. Only 0.1 wt% of MDI-GO was used as a multifunctional crosslinker, which moderately improved the tensile strength, tensile modulus and elongation at break, by 20%, 13% and 5%, respectively. Likewise, similar to Lo and coworkers [69], carboxylic acids on the edges of GO have been reacted with epichlorohydrin to chemically bond with poly(N-isopropylacrylamide-co-acrylic acid) microgel [74]. This dual network of polymer/GO composite exhibited thermal and pH responsiveness with good reversibility, owing to the presence of stable covalent bonds. Kumar and coworkers enhanced the hydroxyl functionality of GO by performing a diazotization, followed by oxidation using tetrakis(2-hydroxyethyl) ammonium chloride [75]. The enhanced hydroxyl-group containing GO was used as a chemical crosslinker with NCO-terminated polyurethane prepolymer without any additional chain extender. Instead of performing a two-step surface modification, McGrail et al. reported a one-step, rapid covalent functionalization of GO or rGO by using the Pinner reaction between hydroxyl groups of GO or rGO with nitriles in acidic aqueous solutions [76]. This simple method requires minimal purification and drying steps and multiple grams of GO can be functionalized in only a couple of hours.

While the majority of research has focused on functionalizing the surface of GO using a variety of chemical agents via “wet” methods, Lee and coworkers irradiated GO with γ-rays to introduce peroxides at the edge of GO flakes. This modified GO not only acted as a crosslinking agent in the system, but also participated as an initiator to polymerize acrylic acid monomers in aqueous solution [77].

CONCLUSIONS AND PERSPECTIVES

A significant amount of effort during the last decade has been committed towards proposing new methods and material combinations for preparing polymer/GO composites. The reality is that, even with the aggressive upturn in research activity during the last decade and high expectations for commercialized products utilizing graphene or GO derivatives, the emergence of products that have reached the marketplace has been slow but steady [78]. Some

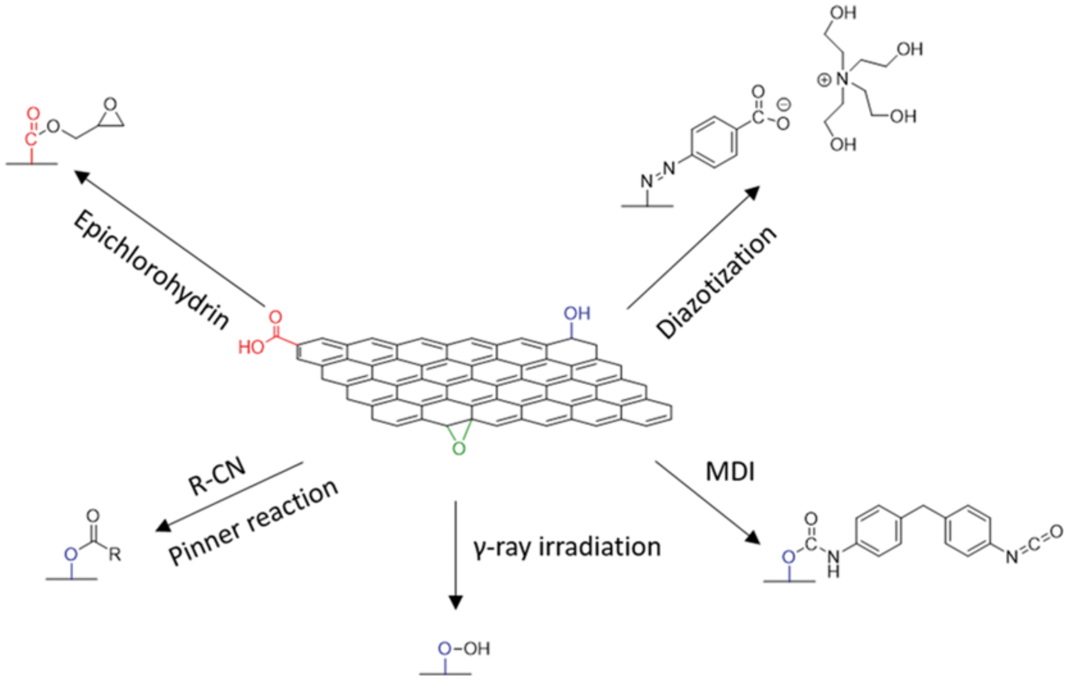

Fig. 13. Miscellaneous surface functionalization methods proposed for GO.

of the challenges that are facing practical implementation of polymer/GO composites include scalability, price, storage and transportation issues, as well as health and safety concerns [3]. Although GO exceeds both the productivity rate and scalability of pristine graphene, both experience emerging concerns on the effect of nanoparticles on human health, which is also a topic of continuous scientific research [79,80]. Nonetheless, a number of these issues are being rapidly resolved through fundamental and applied research, which will only accelerate commercialization activity [81]. As a result, many scientific reports and perspectives project rapid growth and accelerating product launches in the near future.

It is clear that polymer/GO thermosets offer substantial opportunities in many emerging technologies that require a suite of high performance properties, such as mechanical robustness and high thermal/solvent resistance. Owing to its highly oxidized surface, GO can readily serve a dual purpose as a multifunctional crosslinker and property enhancer, with or without additional functionalization. However, there is still a gap in fundamental understanding of the resulting structure-processing-property relationships in polymer/GO composites, primarily due to the wide range of GO sizes, shapes, distributions, surface functionalities and C/O atomic ratios being used. Research directed towards this challenge will continue to benefit both the scientific community as well as commercialization efforts.

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