Graphene functionalization and its application to polymer composite materials

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The progress of graphene research is growing very fast after the discovery of graphene in 2004. This is no doubt that commercialization of graphene will center in the future of graphene. The key challenge is the scale-up production of graphene or graphene-based materials. The hope has been lightened by several breakthrough results introduced above. However, the reproducibility is still concerned, as it is difficult to control the uniformity of individual graphene sheets from “top down” method. It also may be affected by the irregular edge of graphene and randomly dispersed functionalities on graphene sheets. The state-of-the-art techniques are also needed to achieve well-controlled microstructure of functionalized graphene and its derivatives. The article reviewed graphene functionalization and its application to polymer composite materials.

1. Introduction
Graphene, the thinnest material in the world ever, is one-atom-thick carbon sheet consisting of 2D honeycomb lattice. Graphene is the strongest material measured ever with young’s modulus of 1 TPa and tensile stress of 130 GPa, that is, 100 times that of steel. The thermal conductivity of graphene is as high as up to 5000 Wm⁻¹K⁻¹, and theoretical specific surface area is close to 2630 m²/g. The excellence in electrical properties is the major reason for graphene to draw the attention from other 2D materials, in which ambipolar electric properties and quantum hall effects have been demonstrated in graphene. The carrier mobility historically hits a high value of 200 000 cm²/V·S as the electrons transporting across graphene behave like massless relativistic particles. There is no doubt graphene has been labeled with most wonder material ever to scientific community and believed to become an exciting multidiscipline platform attracting physicists, chemists and engineers together to bring storming revolution to the technologies currently used in this society.

However, the most difficult thing for handling graphene is that suspended graphene is unstable and tends to stick together though suspended graphene can exist. Functionalization of graphene is considered as the main route to make suspended graphene stable in complex environment with introducing a third party into graphene surface via chemical or physical approaches. It is believed that this will play a key role when moving graphene from lab benches to real applications. The progress on functionalizing graphene goes very fast after quick learning from carbon nanotubes (CNTs) due to both the carbon materials have similar chemical structure.

2. Functionalization of graphene
It is worthy looking at the electronic structure of graphene to source the roots of graphene for functionalization. The basic chemical unit of graphene is hexagonal rings consisting of carbon atoms in sp² hybridization state. The carbon atoms are covalently connected with each other by σ bonds as result of pairing one electron in 2p orbital. Another electron in 2p orbital is delocalized across the carbon atoms to form π bonds. Thus, graphene, to some extent, can be viewed as a conjugated macromolecule. Noncovalent functionalization of graphene exhibits the advantage in preventing conjugated structure from the damage.

The theory of organic chemistry provides a box of tools to treat the π bonds in graphene with the purpose of introducing functional groups. Oxidization of graphite should be the most common approach to generate oxygen-based functional groups onto graphene sheets. It gives the chance to exfoliate graphene sheets in water and organic solvents. It is not difficult for dispersing graphite oxide in water due to the hydrophilic nature of the oxygen groups on the surface of carbon sheets. However, the solubility of graphite oxide in organic solvents is complicated, which triggers the research work to functionalizing graphene initially. With modification of
the Hummers method and use of expandable graphite originally intercalated with sulfuric acid to replace natural graphite as a starting material for oxidation, the resulting graphite oxide can be exfoliated into single-layer graphene oxide (GO) sheets in N,N-dimethyl-formamide (DMF) directly without any chemical treatment, indicating that graphite oxide obtained from this experiment is amphiphilic. Paredez et al. suggested that the organic solvents with higher polarity generally have better dispersing ability. They found that suitable organic solvents to disperse GO, include DMF, N-methyl-2-pyrrolidone, tetrahydrofuran and ethylene glycol. In contrast, some solvents, such as dichloromethane, n-hexane, methanol and o-xylene, failed to accommodate GO at all. Other solvents, including acetone, ethanol, 1-propanol, dimethyl sulfoxide and pyridine, could stabilize GO for very short term from hours to a few days. In general, the introduction of nonpolar moieties such as alkyl chains to graphene is the way to enhance the solubility of graphene in nonpolar organic solvents. Graphene will become amphiphilic after being attached with amphiphilic molecules.

Further chemical treatment of these oxygen seeds including carboxylic, epoxy and hydroxyl groups boils up a large number of graphene derivatives with broader applications. The amidation and esterification taking place at carboxylic sites are commonly used to create covalent linkage with organic moieties containing hydroxyl and amide groups. In some cases, the reactivity of carboxylic groups needs to be activated via coupling reaction with thionyl chloride. The carboxylic/hydroxyl groups were also reported to take the addition reaction with isocyanate derivatives to form the covalent bonds of amide/carbamate ester. As the monoisocyanates are used, graphene can be functionalized with aliphatic and aromatic groups connected to isocyanate groups. The use of di-isocyanate derivatives can lead to the introduction of a living isocyanate groups onto graphene, providing further chance to functionalize graphene with organic molecules and polymer chains. The epoxy groups on GO can be converted to hydroxyl groups after following nucleophilic ring-opening reaction with amine groups.

The radical reaction is another route to open π bonds for the attachment of functional groups. It is not difficult to source the ways to produce radicals from well-established knowledge in the past typically featured with the thermal decomposition or photolysis of organic peroxides or azo compounds and redox reaction of hydrogen peroxide and iron. The chemical tails of the radicals will become the functional attachment onto graphene. Moreover, Shen et al. found that the radical on the surface of graphene could be terminated by oxygen or carbon dioxide in the air, by which it was claimed as a new possible way to make graphite oxide.

Electron-transfer chemistry can be used to understand the reaction between graphene and diazonium salt, resulting in covalent attachment of aryl groups to the basal carbon atoms. Sharma et al. found that single-layer graphene was almost ten times reactive than bi- or multi-layers of graphene, and, at first time, observed that the reactivity of graphene edges was at least two times higher than that of central interior of single graphene sheet. All these reactivity differences were down to the density of electronic states, which determined electron-transfer rates in different situation. Graphene was thermally unstable, and the hydrogenation also found to be reversed at a high temperature of 450°C. Fluorination of graphene could be carried out by directly exposing graphene to fluorine gas such as xenon difluoride or generating active fluorine atoms by plasma treatment of fluorine gas (CF4 and SF6). Other routes for the addition of graphene include nitrene and 1,3-dipolar cycloaddition of graphene by using azido-phenylalanine and azomethine ylides, respectively.

For technological aspects, the functionalization above requires pre-exfoliation of GO or graphite, otherwise functional groups only can be attached to the carbon layers outside. Consequently, the yield is limited. Englert et al. developed a much more efficient method for covalent bulk functionalization of graphene. First, the reductive treatment of graphite with solvated electrons was performed in an inert solvent of 1,2-dimethoxyethane (DME) by using the liquid alloy of sodium and potassium as a very potent electron source. During this process, solvated electrons were formed to be absorbed into the layers of graphene until saturation was reached. At the same time, solvated potassium was intercalated into interlayer galleries to balance negative-charged graphene layers. The expansion of gallery spacing resulted from the dissolution of potassium cations. After the depletion of the potassium source, charged graphene layers were subsequently exfoliated due to electrostatically repelling forces followed by diazonium functionalization.

It is generally clear that π electron pairs on graphene are vulnerable sites by the attack of chemical species. In the theoretical aspect, computational modeling work is also developed alongside experimental trials to have deeper understanding on the formation of the functional attachments in atomic level. Taking hydrogenation of graphene as an example, it was believed that chemisorption of hydrogen atom resulted in the transformation from sp2 to sp3 hybridization via breaking one of π bonds, and meanwhile an unpaired electron was created to remain at the neighboring carbon atoms. Geometrically, an intermediate form of sublattice was formed in graphene by the introduction of C-H bond, which showed that the values of length and angle of C-C bonds was in between that for sp2 and sp3 C-C bonds. Due to the “delocalized” characteristic of the π-orbitals in graphene, the unpaired electron was smeared in one of the sublattice to make carbon and hydrogen atoms magnetic. This intermediate state was not stable, and next hydrogen atom would quickly terminate the unpaired electron and recover energetic equilibrium. In order to minimize geometric frustration, it was also demonstrated that atomic distortion was seriously produced inside the circle with the radius of 5 Å equal to two periods of graphene crystal lattices, which was less strong beyond this circle. For the energetic stability with minimal additional distortions, the next hydrogen atoms in graphene preferred...
to be chemisorbed by neighboring carbon atoms at another side of graphene sheets. The computational study on imperfect graphene showed that the defects inside graphene were supposed to be the center of chemical activity as both the chemisorption and activation energies of imperfect graphene were calculated to be lower than ideal graphene.29 The studied defects included stone-wales defects, bivacancies and nitrogen substitution impurities. Thus, it was easier for the chemisorptions of the first hydrogen atom on the defects. However, the energy barrier existed for the location of the second hydrogen atom as the local energy minima were formed during the first step, and it prevented further functionalization in addition to the defective sites. It was also pointed out that the presence of unpaired electron due to broke bonds was considered as the reason for the graphene edge to have higher chemical activity than bulk graphene. Similar computational studies were also applied to understand the functionalization of graphene by other chemical species in atomic level.

Grafting macromolecules onto graphene has also generated a great deal of interests since the macromolecular chains are showing improved thermal stability and exhibit stronger steric hindrance to prevent the aggregation of graphene in comparison with the functional groups. Furthermore, it allows covalent integration of graphene into more complex organic system to develop novel composite materials. After quickly learning from the stories of CNTs, the research in this field has been developed on a fast track. It was favored by some researchers to divide these strategies into two categories: “grafting from” and “grafting to” methods.30 The key difference lies in the “grafting from” methods concerned with the growth of macromolecules initiated from the surface of graphene, and “grafting to” methods are about linking presynthesized macromolecules to graphene.

In terms of “grafting from”, atom-transfer radical polymerization (ATRP) has shown great advantages in controlling the structure of polymers. The initiating seeds can be kept alive and hardly experience termination by the impurity from environments in comparison with anionic or ionic polymerization. Copolymer can be designed with controlled length of blocked segments. It is interesting to have the terminal alkyl halide converted to diverse functionalities via organic chemistry. Lee et al. reported31 a typical ATRP procedure to graft the graphene with polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(butyl acrylate), respectively, in which 2-bromo-2-methylpropionyl bromide (BMPB) played as the initiator. The key step was binding BMPB with the surface of GO via the esterification-like reaction of the acyl bromide in BMPB with the hydroxyl groups in GO. Other researchers also studied other ways for the connection of the initiator with graphene. Gonçalves et al.32 used ethylene glycol to terminate the carboxylic groups in GO for the enrichment of the hydroxyl groups followed by the similar route as reported in Ref. 31. Yang et al.33 attempted to convert the carboxylic groups to amine groups that could work with the hydroxyl groups together for the attachment of the initiator. It was found that poly(2-(dimethylamino)ethyl methacrylate) chains grown onto the surface of graphene could assist the carbon sheets to accept poly(ethylene dimethacrylate-co-methacrylic acid) particles via the interaction of hydrogen bonding. Fang et al. argued that it should take more caution when decorating reduced GO (rGO) with ATRP due to the aggregation tendency of rGO. The stabilization could be compromised by the degree of reduction, size of graphene sheets and extra help from surfactants.34 The following study by the same authors disclosed that the rGO could be covalently attached with hydroxyl groups via the diazonium reaction, and subsequently the grafting density could be controlled by varying the concentration of diazonium compounds.35

Other “grafting from” routes previously appearing in the research of CNTs were also taken into the account for graphene. Shen et al.36 reported a route of In situ free-radical polymerization for grafting rGO with a PS–polyacrylamide (PAM) copolymer. Sp² bond in rGO joined in the copolymerization with styrene and acrylamide initiated by benzyl peroxide. Huang et al.37 investigated the grafting GO with polypropylene chains using In situ Ziegler-Natta polymerization. The oxygen groups allowed the settlement of Mg/Ti catalyst onto single GO sheet in nanoscale. Deng et al.38 proposed a protocol following single-electron transfer in radical polymerization. Wang et al.39 grafted GO from the monomers of acrylic acid and N-isopropylacrylamide (NiPAAm) using Ce(IV) induced redox polymerization initiated by the redox pair of Ce⁴⁺ and hydroxyl groups on GO. Etmimi et al.40 linked the hydroxyl groups on GO with dodecyl isobutyric acid trithiocarbonate (DIBTC) by esterification. With the azobisisobutyronitrile as radical initiator, DIBTC acted as chain transfer agent for reversible addition-fragmentation chain transfer polymerization of PS on the surface of GO. Apart from the routes of living radical polymerization, polyurethane (PU) chains can grow from the hydroxyl and carboxylic groups on GO following the route of polycondensation.41

Lin et al.42 investigated covalent polymer functionalization of GO. A covalently bonded polyethylene-grafted GO hybrid material was fabricated successfully. Schematic of synthetic route was given in Figure 1. γ-Aminopropyltriethoxysilane (APTES) was firstly coated onto the GO sheets, and then maleic anhydride-grafted polyethylene (MA-g-PE) was grafted onto the APTES-coated GO sheets, which were confirmed by means of Fourier transform infrared (FTIR), X-ray photoelectron and differential scanning calorimetry techniques. Functionalization resulted in 96 wt% polymer grafting efficiency, and a 10°C increase in the crystallization temperature, compared with that of the pure MA-g-PE. A dramatic core-shell structure for the functionalized GO sheets was observed by using transmission electron microscopy (TEM) (Figure 2).

The essence of “grafting from” methods is mainly about immobilizing initiators on the surface of graphene available for further polymerization. The principle of “grafting to” methods seems simpler, which requires that either graphene or polymers have the functional
groups with the potential to form covalent linkages. In “grafting from” methods, polymers are the minority compared with graphene and act as dispersants to enhance the compatibility of graphene with organic solvents or polymeric matrices. In most cases, “grafting to” methods is more likely to integrate graphene into polymeric matrices to form composites with covalent interfaces. A review conducted by Salavagione et al. summarized the work related to “grafting to” methods. Esterification/amidation is applied to covalently link the carboxylic groups on GO with the polymers containing hydroxyl or amine groups such as polyethylene glycol (PEG), poly(vinyl alcohol) (PVA), polyvinyl chloride, poly(ethyleneimine), triphenylamine-based polyazomethine and poly(3-hexylthiophene). Nitrene chemistry was reported to simply generate covalent linkage via cycloadditions of azide groups on the end of polymers (PEG, PS and polyacrylate) with C=C bonds in graphene. Ring-opening reaction of epoxides is commonly used to form covalent bonding between epoxy and graphene prefunctionalized with amine groups. This type of reaction also can be applied to open the epoxides on graphene sheets by amine groups on polymer. Sometimes, reactive third party is introduced to react with both polymer and functionalized graphenes (FG), for example the covalent bonding can be formed via esterification of epichlorohydrin with the carboxylic groups in poly(NIPAAm) (PNIPAM) and GO. In another study, grafting PNIPAM to graphene could be achieved by atom-transfer nitroxide radical coupling of Br-terminated PNIPAM and 2,2,6,6-tetramethyl-piperidine-1-oxyl-modified graphene catalyzed by CuBr/N,N’,N’,N”-pentamethyldiethylenetriamine system. Click chemistry (1,3-dipolar azide-alkyne cycloaddition) is also powerful in

![Diagram of synthetic route](image-url)
the “grafting to” method. Kan et al. reported a more universal approach for preparing 2D molecular brushes by grafting macromolecule to graphene via radical coupling.52 The macromolecular radicals were simply prepared by free-radical polymerization of monomers including glycidyl methacrylate, MMA, hydroxyethyl acrylate, methyl acrylate (MA), butyl methacrylate, hydroxyethyl methacrylate, styrene (St), acrylamide and NIPAAm. The solubility of graphene in different solvents could be flexibly controlled with these macromolecular brushes. The similar strategy was applied to prepare amphiphilic graphene by grafting with amphiphilic PS-PAM.12

Functionalization of graphene with inorganic nanoparticles has won a huge amount of focus due to their magic properties. A great deal of research has shown that they can be absorbed onto the graphene to act as inorganic functional species. Metal oxide and metal nanoparticles are studied in most cases. This type of functionalization is leading to a group of novel inorganic–inorganic composites for energy-related application. This part will discuss several popular strategies involved with various interaction forces that drive this absorption process to occur spontaneously.

Direct mixing is usually applied to functionalize graphene with presynthesized nanoparticles using organic compounds as binders. Electrostatic interaction plays as the key driving force when graphene and nanoparticles are both oppositely charged. Sun et al.13 prepared a graphene dispersion stabilized by Nafion with fluorobackbones and found that commercial TiO2 (P25) was bound to negatively charged graphene due to electrostatic attractive force. Yang et al.54 reported another strategy driven by mutual electrostatic interaction, in which Co3O4 nanoparticles were positively charged by grafting with amipropyltrimethoxysilane followed by self-assembling to negatively charged GO. Hong et al.55 charged gold nanoparticles and graphene using 1-pyrenebutyrate (positive) and 4-dimethylaminopyridine (negative), respectively. Then, self-assembly of the gold nanoparticles onto FG was simulated by the mutual electrostatic attraction. π–π interaction was another driving force specifically for assembling of the nanoparticles attached with benzene rings onto graphene. Feng et al.56 used benzyl mercaptan to introduce benzene rings to the surface of cadmium sulphide (CdS) quantum dots. It was believed that the attached benzene rings interacted with rGO via π–π interaction, resulting in the deposition of quantum dots onto the graphene. In addition, Liu et al.57 took the advantage of the adhesive characteristic of polymer to assist graphene to capture nanoparticles. GO was reduced and decorated by bovine serum albumin that is an amphiphilic biopolymer. “Adhesive” graphene could be glued with single or mixed type of nanoparticles. TEM images58 in Figure 3 shows the morphology of the graphene sheet coated with polyhedral oligomeric silsesquioxane (POSS) nanoparticles, and the density of POSS nanoparticles on the surface could be well controlled by this method. The schematic route for the attachment of POSS is illustrated in Figure 4.

In terms of gold nanoparticles, Muszynski et al.59 chemically reduced HAuCl4 with NaBH4 in graphene-octadecylamine suspension. Octadecylamine was chemically linked to GO for improving the solubility of graphene sheets in the solvent of THF. It was considered that simple physiosorption resulted in coating gold nanoparticles...
onto graphene spontaneously. Xu et al.\textsuperscript{60} reported a similar absorption mechanism. A mixture of water and ethylene glycol was used reducing metallic salts to form noble metal nanoparticles (Au, Pt and Pd) in presence of GO. After deposited onto GO, it was found that the metal nanoparticles played a catalytic role in reduction of GO with ethylene glycol to form graphene nanomat to support metal nanoparticles. Guo et al.\textsuperscript{61} attempted to deposit two kinds of metal nanoparticles (Pt and Pd) onto rGO. In this method, H$_2$PdCl$_4$ was reduced by formic acid followed by second reduction of K$_2$PtCl$_4$ with ascorbic acid. Pt nanoparticles grew onto the surface of Pd to form Pt-on-Pd bimetallic nanodendrites with an average size of 15 nm. They exhibited much higher electrocatalytic activity toward methanol oxidation reaction than the platinum black and commercial E-TEK Pt/C catalysts. Li et al.\textsuperscript{62} found that the carboxylic groups in GO could be coupled with a reducing agent that was amino-terminated ionic liquid through the interaction between -COOH and -NH$_2$. It made the
carboxylic groups act as the nucleating sites for the growth of gold nanoparticles. As a result, the coating density of gold nanoparticles could be flexibly controlled by reducing GO or increasing carboxylic content by using 3,4,9,10-perylene tetracarboxylic acid (PTCA) to functionalize GO via π–π interaction. Zhou et al.65 revealed a new depositing method without using organic reducing agent. GO or rGO was coated onto 3-APTES-modified Si/SiO$_2$ substrates, respectively. The oxygen functionalities on graphene immobilized with Ag$^+$ served as nucleation sites, and the growth of Ag nanoparticles occurred owing to the reduction of Ag$^+$ by the electrons supplied by conjugated domains of GO or rGO. Kong et al.64 proposed a similar mechanism for depositing Au nanoparticles on rGO. It was believed that the electron-induced reduction likely resulted from galvanic displacement and redox reaction due to relative potential difference between rGO and Au$^+$. Further to this discovery, the gold nanoparticles formed could be used as seeds to further initiate the growth of gold nanorods on the surface of rGO from the solution of cetyltrimethylammoniumbromide, HAuCl$_4$, and ascorbic acid.65

In addition, CuO,66 SnO$_2$67 and MnO$_2$ nanoneedles68 were deposited onto graphene sheets following the similar route. In some work, microwave was applied to initiate the process of hydrolysis.69 However, it was found that depositing efficiency was significantly limited by low number density of the oxygen functionalities. Wang et al.70 used an ionic surfactant, sodium dodecyl sulfate (SDS), to improve the number of negative charge on the surface graphene. The hydrophobic tails of SDS were absorbed into surface of graphene sheets and hydrophilic sulfate heads were strongly bonded with TiO$_2$ precursors. The number of TiO$_2$ coated to graphene was improved compared with the case without SDS. In a hydrothermal process, Co$_3$O$_4$ nanoparticles were coated graphene by heating up Co(OH)$_2$/graphene composites at 450°C following the reaction of Co(NO$_3$)$_2$ and ammonia.71

3. **Application to polymer composite materials**

Graphene is holding a big expectation to tackle several key technological challenges in the industries of aerospace, automotive, defense, electronics and energy.72,73 The functionalization provides one of key tools to deliver graphene as an engineering material. GO is a great ambassador of FG. The door to mass production of graphene is first opened by oxidizing graphite followed by the reduction of GO. Although the quality of rGO is still being argued, researchers have sensed the bonus of the functionalization of graphene, which allows the formation of graphene-based composites. FG has the chance to be dispersed in a variety of solvents due to the existence of the organic attachment. It is easy to figure out a solvent-assisted method to fabricate FG-polymer nanocomposites (FPNs) by selecting the right solvents compatible to polymer and FG. GO is a typical FG usually used in FPNs. Numerous polymers have been incorporated with the FG via this simple method, such as PMMA,74 PU,75 PVA,76 PS77 and polycaprolactone78. In situ polymerization of prepolymers or monomers in presence of the FG is a synthetic approach to prepare FPNs. Thermosetting of epoxy in presence of the FG is a typical example for this method.79 In situ emulsion polymerization of styrene monomers in presence of the GO nanosheets exfoliated in water was reported to prepare FG/PS nanocomposites.80 The methods introduced in Section 3.2 can be used to make FG join in the polymerization and bond with polymeric matrices. Although exfoliation of the FG in solvents is very successful in labs, it is clear to see its limitation for melting processing of FPNs that is a high-throughout approach. Thermal shock of graphite oxide can yield single-layer graphene sheets as the oxygen groups are reduced. These exfoliated GO sheets have been incorporated into polycarbonate (PC) by melt compounding, resulting in the enhancement in the electricity of PC.81 However, minor mechanical improvement might result from weak interface as the oxygen functionalities were eliminated. This problem may be solved by using the GO grafted with macromolecules that shows higher thermal stability than GO. A novel process developed in the group could be the solution to tackle this challenge as well.82 This technology is concerned with coating polymer powders such as polyethylene, polypropylene and nylon powders with exfoliated FG in water or organic solvents. After removal of the liquids, the powders coated with the FG are eligible for being processed via twin-extruder and injection molding.

As the strongest materials ever measured, the breaking strength and Young’s modulus of graphene reaches 42 Nm$^{-2}$ and 1 TPa, respectively. However, it is believed that the FG can do a better reinforcing job than pristine graphene as the strength of the interface is central to the mechanical enhancement of PNCs instead of the intrinsic strength of nanofillers themselves. The organic functionalities are capable of enhancing the compatibility between graphene and polymeric matrices, for example via hydrogen bonding. In addition, wrinkled surface of graphene can mechanically interlock with polymer chains to improve the interface. Owing to these interactions, Ramanathan et al.83 found that the PMMA chains were restricted to confined polymeric regions on the substantial surfaces of each exfoliated sheets. The percolation of the confined regions resulted in an unprecedentedly increase in the glass-transition temperature (T$\_g$) of PMMA. Elastic modulus and ultimate strength of the PMMA were improved by nearly 80 and 20%, respectively, with the incorporation of 1 wt% FG. The excellent reinforcing effect of GO was also found in PVA system due to hydrogen bonding between PVA and GO.84,85 The reinforcement also could be attributed to graphene-nucleated crystal-line interface as the increase in the crystallinity of FG-filled PVA was observed.86 More effective interface can be engineered when the FG is covalently bonded with polymeric matrices. Highly stiff PU nanocomposites was achieved due to strong covalent interface resulting from the reaction between the hydroxyl groups on FG and the isocyanate group on the end of PU chains.87 The Young’s modulus of the PU has been improved by nearly nine times with the addition of 4-4 wt% FG. In nanoscratch test, the scratch depth...
of the indenter in materials is recorded along with the scratch length at a certain scratch rate, which reflects the protective ability of the surface coatings for the substrates. The scratch depth profiles in Figure 5 reveal that the incorporation of 4-4 wt% FG resulted in a nearly 80% decrease in the scratch depth. The remarkable improvement in scratch resistance pointed to the promising application of these composite materials in surface coating. In a silicone system, it was found that hydroxyl groups on the FG could covalently bonded to the SiH-containing component during curing silicone elastomer. The modulus of the silicone foam with 0.25 wt% FG increased by over 200% in comparison with pure silicone foam. Rafiee et al.\textsuperscript{79} reported that only 0.125 wt% FG resulted in a remarkable increase in the fracture toughness and fracture energy up to ~65 and ~115%, respectively. In addition, the reduction in the rate of crack propagation in the epoxy reached ~25-fold as a result of the addition of 0.125 wt% FG. It was considered that the 2D structure and wrinkled surface enabled graphene to deflect cracks far more effectively than 1D CNTs or low-aspect-ratio nanoparticles. NASA and Princeton researchers\textsuperscript{85} disclosed a similar investigation on FG/epoxy nanocomposites. However, the toughness of the nanocomposites seemed not to be improved with the addition of the FG up to 0.5 wt%. The addition of 18C-modified FG significantly reduced the toughness of the epoxy. FG-induced toughening is confronting similar complication like the other nanofillers. More experimental and theoretical work needs to be carried out to fully understand the toughening mechanism, which will be one of the core issues in the mechanical enhancement of FPNs in the future.

Rafiq \textit{et al.}\textsuperscript{86} developed nylon 12/graphene nanocomposites. The effect of FG on the mechanical properties, especially toughness, of nylon 12 was investigated. The results revealed that the incorporation of a very small amount (about 0.6 wt%) of the FG caused a significant improvement in ultimate tensile strength, elongation, impact strength and toughness. With 0.6 wt% FG ultimate tensile strength and elongation at break of the nylon 12 are improved by ~35 and ~200%, respectively. The $K_{IC}$ of the nylon 12 is ~1-28 MPa.m$^{0.5}$, and the incorporation of 0.6 wt% FG causes a significant increase of 72% (~2.2 MPa.m$^{0.5}$). 0.6 wt% FG also causes a significant improvement of 175% in impact failure energy of the nylon 12. The incorporation of FG resulted in an increase in amount of $\gamma$ phase of nylon 12, which could be the direct reason for the increase of toughness. Figure 6 shows SEM images of the fracture surface of the FG (0.6 wt %)/nylon 12 composites. Figure 7 shows the impact failure energy obtained from IFWTT.

Although functionalization of graphene is necessary for the issue of dispersion, the FG with destructive conjugated structure contributes little to the conductivity of FPNs. Reduction of FG premixed in polymeric matrices is the way out for achieving conductive FPNs. In a strict way, rGO should be intermediate between pure graphene and FG since minor amount of oxygen groups still remain on carbon sheets after reduction although it is referred to “graphene” in some articles. Ruoff and his coworkers\textsuperscript{77} firstly used rGO to improve the conductivity of PS. The solubility of the isocyanate-modified GO in an organic solvent paved the way to good dispersion of the graphene sheets in the PS matrix. The chemical reduction of the
GO using hydrazine was carried out in presence of the PS to avoid reaggregation of the rGO with minor amount of functionalities. The percolation threshold was found to be as lower as 0·1 vol%, and the maximum electrical conductivity of the nanocomposites could reach 0·1 S/m with the addition of 1 vol% rGO. Low percolation threshold and high value of maximum electrical conductivity are two goals in the development of semiconductive PNCs. It has been clear that the percolation threshold depends on the aspect ratio of nanofillers and the free space for the settlement of nanofillers. A latex technology has been reported to reduce the free space for nanofillers in a PS matrix.85 The concept was simply achieved by mixing dispersion of surfactant-stabilized graphene and PS latex in water. During film formation of PS latex, the graphene would be pushed to the free space between PS latex to form conductive pathway in the PS matrix instead of being randomly dispersed. Through this method, the percolation threshold could be lowered down to 0·6 wt%. The maximum electrical conductivity generally is limited by two factors: the intrinsic conductivity of the nanofillers and electron loss in the junctions of the conductive pathway formed by the nanofillers in polymeric matrices.87 The rGO is conductive, but its conductivity is not comparable with the pure graphene. Mechanical cleaving pristine graphene from graphite in organic solvents has shown its advantage to fabricate quality graphene with high conductivity.88 However, low yield of production will be the limit in real application. The latter factor is not avoidable in PNCs since polymer chains may easily penetrate into the junctions and increase the electron loss transferring through nanofiller networks. This is the reason why the maximum conductivities of PNCs are commonly 2–4 orders of magnitude lower than intrinsic conductivities of the nanofillers.

Solvent-free processing of semiconductive FPNs might be more welcomed by the industry. Kim et al.89 melt compounded polyester with the FG prepared by partial pyrolysis of graphite oxide and achieved a low percolation threshold of 0·3 vol%. This value was much lower than that was required for graphite (3 vol%). Ansari et al.90 also investigated the percolation threshold of poly(vinylidene fluoride) melt compounded with the FG and expanded graphite, respectively. The percolation threshold for expanded graphite was around 5 wt% that was 2·5 time that for the FG (2 wt%). However, Steurer et al.91 found the maximum conductivities of some thermoplastics melt compounded with these FG failed to outperform other conductive carbon fillers such as carbon black and expanded graphite (both have been commercial products for long time). Another similar study disclosed that the rGO also underperform
commercial CNTs. For this reason, the FG may lose the battle to carbon black and expanded graphene nanocomposites (GNPs) for semiconducting PNCs. If the FG wants to be the main player in the future, fabrication of highly conductive FG with low cost will be the goal there.

It has been confirmed that nanofillers can play as barriers to prevent the propagation of heat generated from external environment in polymeric matrices, resulting in improved thermal stability of polymers. The study on the thermal stability of graphite oxide by thermal gravimetric analysis showed that graphite oxide started to lose some mass below 100°C and the elimination of oxygen functionalities and the sublimation of carbon backbone occurred at 248 and 652°C, respectively. The graphene grafted with polymer chains showed better thermal stability than graphite oxide. The onset decomposition temperature of PS-FG was much higher than that of graphite oxide. So further functionalization of GO will extend the application of FG when some polymer needs to be processed at high temperature. Regarding the thermal stability of FPNs, it was reported 1 wt% GO can improve the thermal degradation temperature of PMMA from ~285°C to ~342°C. The thermal degradation temperature of silicone foam increased by 57.7°C, from ~450°C to ~507°C, as 0.25 wt% GO was added.

High thermal conductivity of graphene has simulated researchers to explore the application of FPNs as thermal management materials. The story from the CNT/polymer nanocomposites has informed that the strong phonon scattering in the interface destroys the hope to use small amount of highly conductive CNTs to achieve substantial enhancement in the thermal conductivity of polymers. Some unique composite structures are designed to reduce the interfacial strong phonon scattering. Similar results are found in FPNs. The addition of the GNPs to very high level is the dominant approach to reduce interfacial thermal resistance and yield a desirable value of the thermal conductivity. However, the high loading of graphite can be afforded by low cost of graphite in comparison with expensive CNTs. Yu et al. exfoliated chemically intercalated graphite by a quick thermal shock at high temperature into slightly oxidized GNPs, which were still thermally and electrically conductive. Twenty-four hour sonication was further applied to yield good dispersion of the GNPs in epoxy matrix. The thermal conductivity of epoxy was improved to be 6.44 Wm⁻¹K⁻¹, as 25 vol% GNPs was added. Multilayer GNPs beat CNTs in improving the thermal conductivity of polymers for following factors as suggested by authors: The GNPs with flat surface and large surface area could form stronger interactions with polymeric matrices than CNTs. The rigid GNPs could keep their high aspect ratio in comparison with flexible CNTs. Later, they created a unique microstructure to reduce the interfacial phonon scattering by using the combination of single-walled CNT (SWCNTs) and graphene nanocomposites (GNPs) as a hybrid nanofiller for epoxy. It was suggested that flexible SWCNTs could bridge planar GNPs via Van der Waals attraction and extend the contacting area of SWCNT-GNP junctions for more phonon transfer. A synergistic effect of the hybrid nanofiller was presented in the enhancement of the thermal conductivity of epoxy nanocomposites. The optimum combination was 1:3, and the optimum loading of the hybrid filler should be in the range of 10–20 wt%. The synergistic effect disappeared as the addition of the hybrid fillers was over 30 wt%. Ganguli et al. found that 20 wt% silane functionalized thermally expanded graphite enhanced the thermal conductivity of epoxy from 0.2 Wm⁻¹K⁻¹ to 5.8 Wm⁻¹K⁻¹. It was found that silane functionalities could form covalent bonding with epoxy and improve the interfacial heat transfer between two components by reducing acoustic impedance mismatch in the interfacial area. It is important to investigate if high loading of GNPs would seriously affect the ductility of polymers. Vega et al. thermally expanded graphite by applying alcohol and oxidative acid treatment with the assistance of long time and vigorous sonication, by which the carbon nanosheets was well dispersed in epoxy matrix with a thickness less than 10 nm. The incorporation of 33 vol% carbon nanosheets could improve the in-plane thermal conductivity of epoxy nanocomposites to 80 Wm⁻¹K⁻¹, which was five to ten times that of the average value across plane direction. This highly anisotropic nature resulted from the 2D structure of graphene sheets. Interestingly, the epoxy nanocomposites still had good ductile properties even with 33 vol% carbon nanosheets.

Wang et al. investigated the effect of FG on the curing dynamics of cyanate ester resin PT-30. The chemical reactions of the systems were analyzed by FTIR and Raman spectroscopies. The incorporation of FG into PT-30 showed a strong catalytic effect on the curing reaction of PT-30, especially at the initiation stage. The initial activation energy and curing temperature greatly decreased. Addition of 4 wt% FG resulted in the decrease of curing temperature of PT-30 about 97°C (Figure 8). Activation energy of the nanocomposites also maintained at a low and constant level till the end of the curing. The most effective catalytic was observed at 1 wt% of the FG. Both FTIR and Raman spectra revealed the chemical reactions in FG and PT-30 systems. –OH of FG reacted with cyanate group O-C=N and formed O2-C=NH bond at the early stage of the curing process. This was regarded as the nature of the catalytic effect of FG. These results provide a low-temperature curing route of cyanate ester resins with improved curing efficiency.

Electroactive polymers are a new generation of “green” cathode materials for rechargeable lithium batteries. Wang and his workers have developed nanocomposites combining graphene with two promising polymer cathode materials, poly(anthraquinonyl)sulfide) and polyimide, to improve their high-rate performance. The polymer–graphene nanocomposites were synthesized through a simple In situ polymerization in the presence of graphene sheets. The highly dispersed graphene sheets in the nanocomposite drastically enhanced the electronic conductivity and allowed the electrochemical activity of the polymer cathode to be efficiently utilized. This allows for ultrafast charging and discharging; the composite
The onset of curing temperature decreased dramatically for the nanocomposites. A less reduction of the temperature was observed at 2 wt% of the FG. On the contrary, the peak temperature continually decreased with the increasing of the FG content. For PT30/4wt% FG nanocomposites, the presence of FG strongly catalyzed the curing reaction. FG, functionalized graphene.

Figure 8. Nonisothermal DSC plots of the PT30/FG nanocomposites. The onset of curing temperature decreased dramatically for the nanocomposites. A less reduction of the temperature was observed at 2 wt% of the FG. On the contrary, the peak temperature continually decreased with the increasing of the FG content. For PT30/4wt% FG system, the peak temperature decreased about 97°C, compared with the pure PT-30. Therefore, the presence of FG strongly catalyzed the curing reaction. FG, functionalized graphene.

can deliver more than 100 mAh/g within just a few seconds. This research is new application being developed quickly in near future.

4. Conclusions and prospective

The progress of graphene research is growing very fast after the discovery of graphene in 2004. This is no doubt that commercialization of graphene will be in the future of graphene. The key challenge is the scale-up production of graphene or graphene-based materials. The hope has been lightened by several breakthrough results introduced above. However, the reproducibility is still concerned as it is difficult to control the uniformity of individual graphene sheets from “top down” method. It also may be affected by the irregular edge of graphene and randomly dispersed functionalities on graphene sheets. The state-of-the-art techniques are also needed to achieve well-controlled microstructure of FG and its derivatives. With numerous investments from many countries, the authors do hope first commercial graphene products can come into reality in near future.

As occurred with other nanofillers, the main challenge in designing graphene-based polymer nanocomposites with maximally enhanced properties is, therefore, to effectively disperse the graphene sheets inside the host polymer matrix. Often, the fabrication of polymer nanocomposites is hindered by the tendency of nanoparticles to form agglomerates. The presence of agglomerates in polymer nanocomposites can negate the advantages of the nanofillers. As known, the nature of graphene makes it hard to disperse within the majority of polymers since it can only interact efficiently with a limited group of polymers typically containing aromatic rings. In addition, the low solubility of pristine graphene also limits its applications. In order to make graphene dispersible in – or compatible with – a variety of polymer matrices, as well as to maximize the interfacial interactions, chemical modification is generally required, introducing functional moieties that confer other properties to the pristine material. Functionalization of graphene has been widely devoted to the production of highly exfoliated graphene sheets in organic solvents, which has opened new horizons of using the nanosheets for developing new kind of polymer nanocomposites. Very active edge functional groups are the advantage for the FG to form a good dispersion and strong interactions with polymeric matrices. To date, various graphene and its derivatives/polymer nanocomposites have been widely produced including PS, PC, polyimides and PMMA and so on by solution mixing and achieved high reinforcement efficiency. Many reports demonstrate that graphene and graphene-based materials with the 2D platelet geometry offer certain remarkable property improvements of polymer matrices combining the lamellar properties of layered silicates with the unique characteristics of CNTs. At very low filler contents, most of these properties were better than those observed for other carbon-based reinforced nanocomposites, especially improved toughness and gas permeation resistance of the composite, due to the higher aspect ratio of graphene. Graphene allow for much lower loading levels than other nanofillers to achieve optimum performance, which significantly impact weight reduction of nanocomposite materials. The versatility of graphene polymer nanocomposites suggests their potential applications in automotive, electronics, aerospace and packaging. Relative to solution mixing, melt blending is often considered as the most economically attractive, scalable and environmentally friendly method for applicable applications. However, use of this method has so far been limited to a few studies because of dispersion difficulty occurs as FG fillers in dried state, which could affect graphene future applications. As known, graphene is a very soft, flexible and transparent 2D sheet. Extent of the graphene wrinkles may be altered by factors, such as composite processing methods and conditions, as well as interaction with the polymer matrix. Weak interfacial interaction between the graphene platelets and polymer matrix could help to present a high wrinkled and flexible structure of the graphene. In addition, the high wrinkled structure could lead to low aspect ratio and result in changes of its effective performance in the polymer matrix. It has been reported that highly crumpled structure has significantly reduced the effective stiffness of the graphene platelets and thus diminish their reinforcing capability. The challenge of application of graphene to polymer materials is still dispersion and transfer of physical properties of graphene to polymer matrices. To overcome the above difficulties, it is believed that functional graphene/polymer nanocomposites shall be applicable in the daily life.
REFERENCES


54. Feng, M.; Sun, R.; Zhan, H.; Chen, Y. Lossless synthesis of graphene nanosheets decorated with tiny cadmium sulfide.
quantum dots with excellent nonlinear optical properties. Nanotechnology 2010, 21, 075601.
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