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7 Graphene/Polymer Composite Materials: Processing, Properties and Applications

Abstract: Graphene, a two-dimensional monoatomic thick building block of a carbon allotrope, has attracted tremendous attention due to its remarkable physical properties and chemical functionalization capabilities. Graphene and its derivatives are potential nanofillers that can dramatically improve the performance of polymer-based composites at an extremely low loading. This chapter presents the state-of-the-art progress in the synthetic methods of graphene and its derivatives as well as their polymer composite materials. Various fabrication processes of graphene and graphene-based polymer composite materials are introduced. The mechanical, thermal and electrical, and other important properties of the composites were also discussed along with their potential applications. This chapter concludes with a brief discussion of the challenge and outlook of the graphene/polymer composites and its future prospects in this rapidly emerging field.

7.1 Introduction

Graphene, one of the allotropes (diamond, graphite, fullerenes, and carbon nanotubes) of carbon family, is a planar monolayer of sp^2 hybridized carbon atoms arranged in a two-dimensional (2-D) lattice. It has been viewed as the basic building block for graphitic materials of all other dimensionalities (Figure 7.1) (Geim, 2007). For example, the fullerenes (buckyballs, 0-D carbon allotrope) can be envisioned to be made by wrapping a section of graphene sheet. The carbon nanotubes (CNTs, 1-D carbon allotropes) can be made by rolling graphene nanoribbon. The graphite (3-D carbon allotrope) is made of graphene sheets stacked on top of each other and separated by 3.37 \AA . Although known as an integral part of 3-D materials, strictly 2-D graphene crystals had been believed to be thermodynamically unstable and not exist, being described to an ‘academic’ material (Fradkin, 1986). Suddenly, isolation of free-standing single-layer graphene was first achieved in 2004 when graphene was separated from graphite using micromechanical cleavage (Novoselov, 2004); and the

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follow-up experiments confirmed that its charge carriers were indeed massless Dirac fermions (Novoselov, 2005; Zhang, 2005). The revolutionary discovery of graphene has been awarded the Nobel Prize in Physics 2010 to Andre Geim and Konstantin Novoselov “for ground breaking experiments regarding the 2-D material graphene” (Singh, 2011).

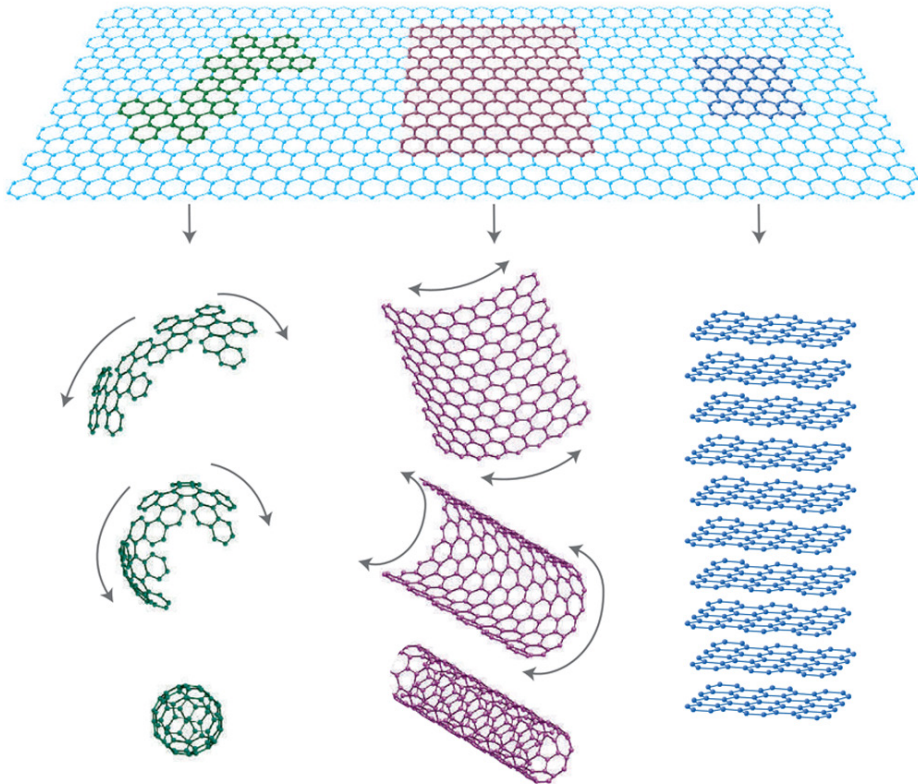


Figure 7.1. Graphene is a 2D building block of all graphitic forms. It can be wrapped to form 0-D buckyball, rolled to form 1-D nanotube, and stacked to form 3-D graphite (Geim and Novoselov, 2007). Copyright 2007 Nature Publishing Group.

During the past decade, graphene sheet and its derivatives have generated great interest and activity in most areas of science and engineering due to their unique structure and unprecedented physical and chemical properties. Graphene has demonstrated the combination of superlative mechanical, thermal and electronic properties, such as the quantum hall effect, high carrier mobility under ambient condition ($\sim 250,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) (Novoselov, 2005; Novoselov, 2004), exceptional thermal conductivity ($3000\text{-}5000 \text{ W m}^{-1}\text{K}^{-1}$) (Balandin, 2008), good optical transparency ($\sim 97.7\%$) (Nair, 2008), high specific surface area ($\sim 2600 \text{ m}^2\text{g}^{-1}$) (Stoller,

2008), and superior mechanical properties with Young's modulus of ~1 TPa (Lee, 2008). To exploit these intriguing properties in practical applications, various synthetic routes have been developed to prepare graphene and its derivatives, ranging from the bottom-up epitaxial growth (Jiao, 2009; Kim, 2009c; Li, 2009; Sutter, 2008) to the top-down exfoliation of graphite by means of oxidation, intercalation, and/or liquid exfoliation (Coleman, 2011; Hernandez, 2008; Li, 2008a; Nicolosi, 2013). To date, graphene-based composites have been successfully made with various inorganic and organic materials, and thus are intensively explored in applications such as batteries (Bai, 2011a; Lin, 2013a; Wang, 2009b; Wang, 2012b; Wu, 2010b; Yoo, 2008; Zhou, 2014b), supercapacitors (El-Kady, 2013; El-Kady, 2012; Stoller, 2008; Wu, 2012e; Xu, 2013b; Zhang, 2013b; Zhao, 2013), fuel cells (Dai, 2013; Mahmood, 2014; Yang, 2012e; Zhu, 2013), and sensing platforms (Abbas, 2014; He, 2010; Li, 2012a; Li, 2013a; Li, 2014b; Lightcap, 2013; Lu, 2009; Lv, 2012; Venkatesan, 2012). In particular, to take full advantage of its properties for applications, integration of individual graphene in polymer to form advanced multifunctional composites is one of the most promising routes (Bortz, 2012; Dikin, 2007; Fang, 2009; Huang, 2010b; Im, 2012; Kim, 2010a; Kim, 2008; Lee, 2013a; Luong, 2011; Rafiee, 2009; Ramanathan, 2008; Shen, 2011; Song, 2013; Stankovich, 2006a; Tang, 2013a; Teng, 2011; Wan, 2014b; Wang, 2009c; Zaman, 2012b), because polymer materials usually have exceptional specific modulus and strength, and wide application in aerospace, automobile and defense industries, etc.

As early as 1950, polymer nanocomposites with exfoliated layered silicate fillers have been developed (Carter, 1950), and nearly forty years later a report demonstrated significant mechanical property enhancement using clay as filler in a nylon-6 matrix (Usuki, 1993), which attracted significant academic and industrial interest in nanocomposites. With the development of nano- science and technology, many nanofillers, such as carbon black, nano-silica and CNTs, have been widely studied and used to improve mechanical, thermal, electrical, and gas barrier properties of polymers. Considering the fact that graphene has a higher surface-to-volume ratio than CNT because of the inaccessibility of the inner nanotube surface to polymer molecules (Stankovich, 2006a), graphene is promising to be more favorable for improving the properties of polymer matrices. In the past few years, graphene and its derivatives have been incorporated into a wide range of polymers, including epoxy (Liang, 2009c), polystyrene (PS) (Pang, 2011), polypropylene (PP) (Song, 2011), polyethylene terephthalate (Zhang, 2010b), polyaniline (PANI) (Yan, 2010a), nylon (Rafiq, 2010) and polymethylmethacrylate (PMMA) (Zhang, 2012a) for various functional applications. However, there are some key issues and challenges for fabricating advanced graphene/polymer nanocomposites. Many factors, including the type of graphene and its derivatives as well as their intrinsic properties, the dispersion and exfoliation of graphene in the polymer, the interfacial interaction between the graphene and the matrix, and the network structures of graphene in the matrix can affect the properties and application of graphene/polymer composites.

Based on recent advancements in the production of different kinds of graphene and their polymer composites, this chapter presents the synthesis of graphene and its derivatives, and narrates the surface modification of graphene with an emphasis on methods suitable for fabrication of polymer composites. Then the properties and applications of graphene/polymer composites are introduced and discussed. Finally, we will conclude with the challenges of the advanced graphene/polymer composites, providing guidance and stimulating development for wider applications.

7.2 Synthesis of graphene

In order to explore the various aspects of graphene/polymer composite materials, the synthetic procedures of graphene and its derivatives will be first described. This section contains a brief introduction to synthetic methods of graphene that are critical to fabricate high-performance graphene/polymer composites.

7.2.1 Bottom-up approaches

Graphene and its derivatives can be prepared by many synthetic methods, which can be generally classified as the bottom-up and top-down approaches (Kim, 2010a). In the bottom-up processes, graphene materials are directly synthesized from the carbon sources by various methods, such as chemical vapor deposition (CVD) (Dong, 2011; Kim, 2009c; Li, 2009; Li, 2011c; Reina, 2008), epitaxial growth on SiC or metals (Berger, 2006; Emtsev, 2009; Gao, 2011; Sutter, 2008), unzipping carbon nanotubes (Cai, 2010a; Jiao, 2010; Jiao, 2009; Kosynkin, 2009). Normally, CVD and epitaxial growth methods can produce tiny amounts of large-size, defect-free graphene sheets. Bae et al. reported a roll-to-roll production of 30-inch graphene films using the CVD approach, and the obtained graphene monolayer films have low sheet resistances with good optical transmittance, showing great potential to replace commercial transparent electrodes (Bae, 2010). They may be more attractive and suitable for fundamental studies and electronic applications but are not applicable for polymer nanocomposites that require a large amount of graphene sheets preferably with modified surface structure. The graphene ribbons unzipping from CNTs show some advantages in size controlled by selection of the starting nanotubes, but the source of nanotubes is still expensive for preparation and application of polymer composites.

7.2.2 Top-down approaches

Unlike the bottom-up approaches, the top-down approaches involve the synthesis of graphene or modified graphene from separation/exfoliation of graphite or graphite derivatives. In general, these methods seem to be more appropriate for large scale production required for polymer composite applications since graphite is a commodity material with current annual global production of over 1-2 million tons. Therefore, starting from graphite or its derivatives (such as graphite oxide (GO) and graphite fluoride) offers significant economic advantages over the bottom-up methods. Herein, two main top-down approaches including directly exfoliated and chemically derived graphene will be discussed in detail.

7.2.2.1 Directly exfoliated graphene

Micromechanical cleavage of graphite is an effective and reliable method to produce large-size, high-quality graphene. Based on such method, many excellent properties of graphene including high electron mobility at room temperature (Bolotin, 2008), exceptional thermal conductivity (Balandin, 2008), and superior elastic modulus and strength (Lee, 2008) have been verified. Unfortunately, the low yield of this approach severely limits its application in the manufacture of polymer composites, which makes it only suitable for fundamental studies or electronic applications (Novoselov, 2004). Recently, graphite has also been directly exfoliated to single- and multiple- layer graphene via sonication or ball milling in the presence of various surfactants (Bergin, 2008; Coleman, 2012; De, 2010; Hernandez, 2008; Viinikanoja, 2014; Zhao, 2010a), such as polyvinylpyrrolidone (Bourlinos, 2009), sodium cholate (Lotya, 2010), electrochemical functionalization of graphite assisted with ionic liquids (Liu, 2008). The direct exfoliation of graphite by sonication has potential to be scaled up to produce large quantities of graphene or functionalized graphene that can be used for composite applications. The schematic description of the liquid exfoliation of layered materials including graphene has been proposed by Coleman and co-workers (Nicolosi, 2013), as shown in Figure 7.2. When the graphite powder is exposed to sonication in the presence of a suitable solvent, and the powder fragments are exfoliated into nano-scale sheets, which are stabilized against aggregation by the solvent. The exfoliated sheets are free of defects and oxides and can be produced in large quantities, showing promise for production of graphene with high-quality in large quantities, although some drawbacks such as separation of the exfoliated graphene from the bulk graphite, the cost of its removal dissolution and low conductivity induced by the residual surfactant are still challenges.

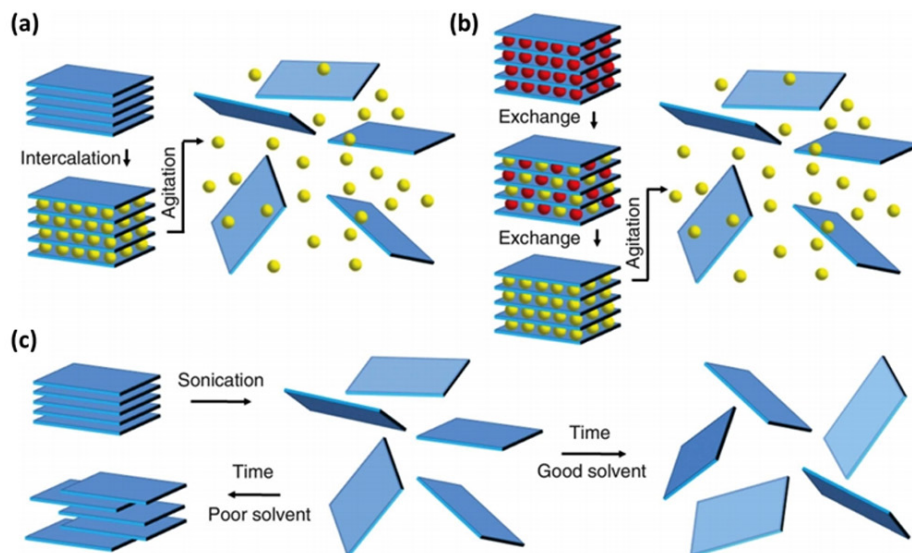


Figure 7.2. Schematic description of liquid exfoliation of layered graphite materials (Nicolosi, 2013): (a) ion intercalation: ions (yellow spheres) are intercalated between the layers in a suitable solvent, swelling the crystal and weakening the interlayer attraction; then, agitation (such as sonication) can completely separate the layers, resulting in an exfoliated dispersion; (b) ion exchange: the ions (red spheres) can be exchanged in a liquid environment for other, often larger ions (yellow spheres); (c) sonication-assisted exfoliation: the layered crystal is sonicated in a solvent, resulting in exfoliation and sheet formation.

7.2.2.2 Chemically oxidized/exfoliated graphene

At present, the most promising scalable method of graphene production is the reduction of highly oxidized graphene oxide from the exfoliated GO sheets, which has emerged to be a viable route to afford graphene-based single sheets in considerable quantities. The GO sheets are usually obtained through the oxidation of graphite using a mixture of potassium permanganate and concentrated sulfuric acid based on Hummers method (Hummers, 1958). Compared to pristine graphite, GO contains various oxygen functional groups including hydroxyl and epoxy groups on the basal plane and carbonyl and carboxyl groups located at the sheet edges on sp^2 hybridized carbon (Stankovich, 2006c). These oxygen groups on the basal planes and edges of GO sheets make them highly hydrophilic and very stable aqueous dispersions (Yang, 2009c). Hence, GO is highly hydrophilic and readily exfoliated in water, yielding stable dispersion. Similar exfoliation degree of GO was also attained in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) and ethylene glycol (Paredes, 2008). The formation of stable graphene oxide colloids in water was attributed to not only its hydrophilicity but also the electrostatic repulsion. Li et al. showed that the surface charges on graphene oxide are highly negative when dispersed

in water by measuring the zeta potential due to the ionization of the carboxylic acid and the phenolic hydroxyl groups (Li, 2008a). Note that the structures of GO and graphene oxide are different, although they have similar chemical properties i.e. surface functional groups (Figure 7.3a). Graphene oxide is a monolayer material produced by the exfoliation of GO. AFM images of GO exfoliated by the ultrasonic treatment in water always revealed the presence of sheets with uniform thickness (~1 nm, Figure 7.3b), while the pristine graphite sheet is atomically flat with the Van der Waals thickness of ~0.34 nm. The increased thickness of graphene oxide sheets are attributed to the displacement of sp^3 hybridized carbon atoms slightly above and below the original graphene plane and presence of covalently bound oxygen atoms. However, graphene oxide is electrically insulating and contains irreversible defects and disorders due to the disruption of the conjugated electronic structure induced by these functional groups (Stankovich, 2006b), but the reduction of graphene oxide could partially restore its conductivity at values orders of magnitude below that of defect-free graphene (McAllister, 2007a; Stankovich, 2007).

Various types of reduction methods have been reported to obtain reduced graphene oxide (RGO), such as the chemical reduction (Gómez-Navarro, 2007; Li, 2008a; Nethravathi, 2008; Qi, 2010; Shen, 2012b; Stankovich, 2006c; Tung, 2009; Zhang, 2010c), thermal reduction (Becerril, 2008; Dubin, 2010; McAllister, 2007a; Schniepp, 2006; Shen, 2013d; Zhu, 2010), photochemical reduction (Huang, 2010a; Li, 2012c; Sun, 2013a; Williams, 2008), photothermal reduction (Akhavan, 2012; Cote, 2009; Mukherjee, 2012; Robinson, 2011), microwave-assisted reduction (Chen, 2010a; Chen, 2010b; Sharma, 2010) and electrochemical reduction (Shao, 2010; Wang, 2009d; Zhou, 2009). Among these methods, thermal and chemical reduction methods are frequently used to reduce GO to RGO through removing the oxide functional groups from graphene oxide surfaces (Gao, 2009). Thermally reduced graphene oxide (TRGO) can be produced by rapid heating of dry GO under inert gas and high temperature (McAllister, 2007a; Schniepp, 2006; Zhu, 2010). The stacked GO can be exfoliated and reduced by heating GO to 1050 °C where oxide functional groups were extruded as carbon dioxide, and the exfoliation took place when the decomposition rate of the epoxy and hydroxyl sites of graphite oxide exceeded the diffusion rate of the evolved gases, thus yielding pressures that exceeded the Van der Waals forces holding the graphene sheets together (Figure 7.3c). According to the AFM studies, the thermal reduction/exfoliation can produce 80% single layer reduced graphene oxide, and about 30% weight loss is associated with the decomposition of the oxygen groups and evaporation of water. The bulk conductivities of the products were measured to be 1000-2300 S/m, suggesting the effective reduction and restoration of electronic structures from GO.

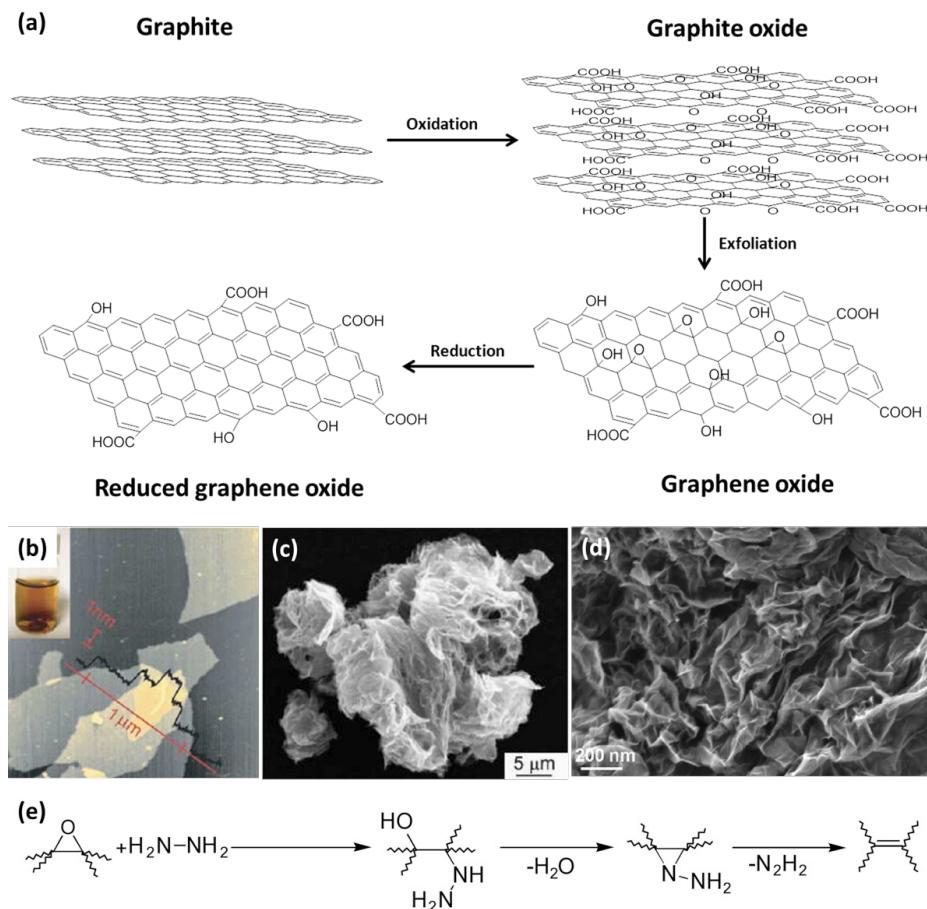


Figure 7.3. Synthesis and microstructure of graphene derivatives: (a) schematic of oxidation of graphite to GO, exfoliation and reduction to graphene oxide and reduced graphene oxide; (b) AFM image of overlapping GO sheets (Stankovich, 2006a): the height profile shows that the thickness of individual GO sheet is approximately 1 nm (The inset shows a photograph of a GO suspension in water); (c) SEM image of TRGO (McAllister, 2007a), showing a structure like crumpled sheets of paper; (d) SEM image of aggregated graphene oxide sheets chemically reduced with hydrazine monohydrate and (e) proposed reaction pathway for epoxy reduction by hydrazine (Stankovich, 2007).

Chemically reduced graphene oxide (CRGO) sheets have been performed by the use of several reducing agents, such as hydrazine (Compton, 2010a; Gao, 2009; Park, 2011; Ren, 2011; Tung, 2009; Yang, 2009a; Zhu, 2011), sodium borohydride (Bourlinos, 2003; Shin, 2009; Si, 2008; Yang, 2012d), strong alkaline media (Fan, 2008), vitamin C or ascorbic acid (Dua, 2010), bovine serum albumin (Liu, 2010), and hydriodic acid (Moon, 2010; Pei, 2010). Hydrazine hydrate was frequently used and found to be the best one in producing very thin and fine graphite-like sheets (Figure 7.3d). Unlike

other strong reductants, hydrazine hydrate does not react with water. During the reduction process, the brown colored dispersion of graphene oxide in water turned black and the reduced sheets aggregated and precipitated. The re-establishment of the conjugated graphene network could be attributed to the reaction pathway (Figure 7.3e) (Stankovich, 2007), and hydrazine takes part in ring-opening reaction with epoxides and forms hydrazino alcohols (Stankovich, 2006b). Li and coworkers further prepared the stable aqueous suspension of RGO sheets by adjusting the pH (with ammonia solution) of the aqueous solution during reduction with hydrazine (Li, 2008a). Comparatively, sodium borohydride is more effective than hydrazine as a reductant of graphene oxide since such reduction produce RGO with lower sheet resistances high C/O ratios measured in the same study (Bourlinos, 2003). Carbon elemental analysis revealed the evidence for the complete reduction of graphene oxide in this process (Bourlinos, 2003; Shin, 2009). Other chemical reduction routes such as strong alkaline media (Fan, 2008), vitamin C or ascorbic acid (Dua, 2010), bovine serum albumin (Liu, 2010), and hydriodic acid (Moon, 2010; Pei, 2010) have also been investigated. While the hazardous nature and cost of the chemicals used in these methods may limit the practical application, although they provide efficient routes for production of RGO sheets.

Despite the fact that the conductivity of RGO is much lower compared to the defect-free graphene due to the presence of residual oxygenated groups and defects, the most promising routes to preparation of graphene for polymer composites start from GO. The reactive surfaces of GO and RGO provide the tunability in electronic and optoelectronic properties via chemical reactions, and the feasibility for polymer composite incorporation. As indicated in the discussion above, the most promising routes to preparation of graphene for polymer composites start from GO, which will be concentrated in the rest of this chapter.

7.3 Processing of graphene/polymer composites

7.3.1 Nature problem of integration of graphene into polymer

Due to low cost and high yield production, GO and RGO as well as their derivatives as fillers for polymer composites have shown a great potential for various important applications, although they have inferior physical properties than perfect single-layer graphene in many cases. In the past decade, research has made successful attempts for GO and RGO filled polymer composites similar to CNT-based polymer composites. According to the difference in starting graphene materials (graphene oxide, TRGO and CRGO), there are three main routes for polymer composites (Du, 2012). Taking a graphene oxide sheet as a starting filler for composites, oxygen groups containing carboxylic, hydroxyl and epoxy groups on the basal planes and edges of sheets make them highly hydrophilic and very stable aqueous dispersions. Thus,

graphene oxide sheets can be easily dispersed in aqueous media for preparation of polymer composites such as epoxy (Yang, 2009c), poly(vinyl alcohol) (PVA) (Liang, 2009a) and poly (allylamine) (Satti, 2010) to improve their mechanical properties and thermal stability (Bortz, 2012; Xu, 2009). Unfortunately, due to the high surface area and strong van der Waals force, the GO sheets in the polymer matrix are still apt to form severe aggregations at a relatively high loading (McAllister, 2007b), and even result in poor sheet/matrix interfacial quality (Wan, 2014b), restricting their application in polymer nanocomposites. Similarly, TRGO and CRGO sheets can easily form irreversible agglomerates or even restack to form graphite through Van der Waals interactions. Therefore, the prevention of aggregation is essential for RGO sheets because most of their unique properties are only associated with individual sheets.

Normally, the vast interfacial area created by nanofillers can influence the behaviour of the surrounding polymer matrix even at a very low content (Desai, 2005), which will affect the neighbouring polymer chains (Bansal, 2005) and, consequently, the performance of the composites. Thus, the performance of graphene/polymer composites is highly dependent on not only the dispersion and exfoliation levels of graphene sheets into the matrices but also their interfacial interactions. As a result, the other important problem remains to achieve strong interface between the graphene and the polymer matrix to promote the stress transferring efficiency (Kotov, 2006). Additionally, other challenges need to be still overcome for the integration of graphene oxide or RGO into polymer matrix (Singh, 2011), i.e. functionalizing graphene oxide or RGO sheets with remaining structural integrity and controlling the folding, crumpling and bending of sheets into the polymer matrix.

7.3.2 Surface modification of graphene

Pristine graphene is hydrophobic in nature and thus cannot be dissolved in polar solvents or polymers, which makes surface modification of graphene sheets important for their future applications. The dispersion of graphene against their agglomeration in solvents and polymer matrixes, after complete exfoliation of graphitic layers, has been achieved by surface modification through non-covalent and covalent bonding.

7.3.2.1 Non-covalent modification

Non-covalent modification with different organic compounds is essential and effective to disperse or exfoliate graphene in solvents and polymers, and thereby avoid the formation of restacking. Non-covalent modification by π -interactions is an attractive synthetic method, because it offers the possibility of attaching functional groups to graphene without disturbing the electronic network (Georgakilas, 2012a),

thus making conductive nanocomposites (Tkalya, 2012). Similarly as previous work on CNT dispersion and surface modification (Fukushima, 2003; Islam, 2003; Kim, 2012; Moore, 2003), non-covalent modification approaches of graphene typically use organic mediating molecules ranging from low molecular weight molecules to supra-molecules to polymers (Choi, 2010; Coleman, 2009; Das, 2012b; De, 2010; Fernández-Merino, 2012; Li, 2008b; Lotya, 2009; Ronan, 2010; Shen, 2009; Yang, 2012d; Zhang, 2013a; Zhu, 2009). Especially, interest in aqueous graphene dispersions is driven by the desire to minimize or eliminate volatile organic compound formulations in many different industrial sectors (Texter, 2014).

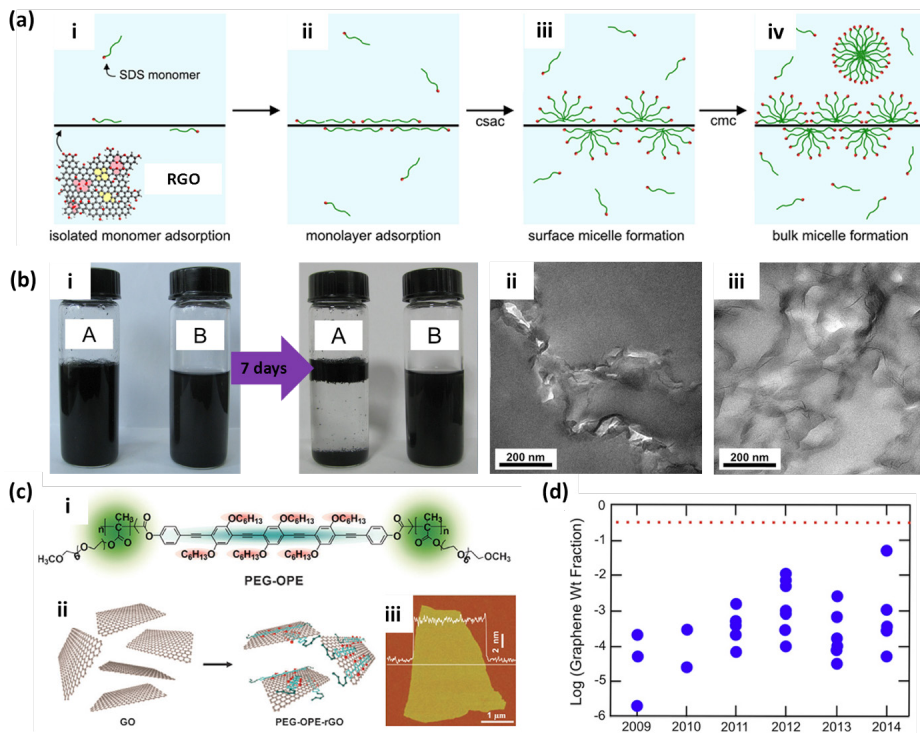


Figure 7.4. Non-covalent surface modification of graphene derivatives: (a) schematic representation of SDS adsorption onto RGO (Hsieh, 2013): (i) adsorption of isolated surfactant monomers, (ii) adsorption of a surfactant monolayer, (iii) formation of hemi-cylindrical surface micelles, and (iv) formation of micelles in bulk solution; (b) Triton X-100 surfactant treated RGO (Triton-RGO) (Wan, 2013): (i) stability of the dispersions after sonication (A: untreated RGO; B: Triton-RGO), TEM images of epoxy composites with 0.2 wt% (a) untreated and (b) treated RGO; (c) triblock copolymer modified graphene (Qi, 2010): (i) chemical structure of PEG-OPE, (ii) schematic illustration of fabrication of PEG-OPE stabilized RGO, (iii) AFM image and cross-sectional analysis of PEG-OPE-RGO on mica; (d) Overview of increase in weight fraction of graphene for exfoliated graphene dispersions in water since early reports (The dotted line at -0.49, corresponding to a weight fraction of about 0.3, represents an upper bound to the amount of graphene that may be able to be dispersed in water.) (Texter, 2014).

The predominant mode of dispersion uses stabilizers (such as surfactants and polymers) to provide steric or electrostatic stability against collision, re-agglomeration or flocculation. For example, to surface-modify graphene by using the ionic surfactant sodium dodecyl sulfate (SDS) were consistent with a four-stage adsorption model (Hsieh, 2013), shown schematically in Figure 7.4a. Adsorption of amphiphilic molecules, such as surfactants and amphiphilic copolymers with hydrophilic or hydrophobic groups, is one of simplest and most effective methods to nondestructively enhance the dispersibility of RGO. Normally, the non-ionic surfactant treatments of RGO were effective method to improve their dispersion stability in water and the dispersion/exfoliation level of sheet in the polymer (Figure 7.4b) (Wan, 2013). The hydrophilic regions of non-ionic surfactants interact with polar solvent molecules, and the hydrophobic regions can adsorb onto nanofiller surfaces (Kim, 2012), and thus facilitate the dispersion stability of nanofillers in water mainly by forming a large solvation shell from the hydrophilic moieties (Kaleemullah, 2012; Ma, 2010; Richard, 2003). Qi et al used a coil-rod-coil conjugated triblock copolymer (PEG-OPE) as π - π binding stabilizer to surface-modify the RGO sheets (Figure 7.4c) (Qi, 2010). Due to the amphiphilicity and π -conjugation of PEG-OPE molecules, the modified RGO form a sandwich structure, making the RGO soluble in a variety of solvents including toluene and water. Recently, Texter deduced the most concentrated graphene dispersions in water to exceed a weight fraction of 0.05, an upper bound of about 0.3, as shown in Figure 7.4d (Texter, 2014), providing great promise for many low cost and high volume processes for producing double layer supercapacitors, highly electrically conducting inks and thin layers, and highly thermally conducting coatings.

7.3.2.2 Covalent modification

Covalent surface modifications feature functional groups or modifier molecules that are attached to graphene by covalent bonds, which includes two general routes (Hsiao, 2010): (1) the formation of covalent bonds between free radicals or dienophiles and C=C bonds of pristine graphene (Georgakilas, 2012b) and (2) the formation of covalent bonds between organic functional groups and the oxygen groups, such as epoxy, carboxyl, and hydroxyl groups, on the surface and edge of the of graphene sheets. In the former route, the functional groups are anchored to carbon atoms in graphene to yield defect carbons in which the hybridization state changes from sp^2 to sp^3 , leading to a loss of conjugation. The introduced defects affect the properties of the graphene sheets, most importantly its electric conductivity. Comparatively, in the latter route, the organic molecules are covalently attached to graphene surfaces without destruction of carbon lattice, showing some advantages for preparation of high performance polymer composites.

Graphene oxide is characterized as a single graphitic monolayer with randomly distributed aromatic regions (sp^2 carbon atoms) and oxygenated aliphatic regions (sp^3 carbon atoms) containing hydroxyl, epoxy, carbonyl, and carboxyl functional groups, which can make them form stable dispersions in water and polar organic solvents

such as DMF, NMP, and THF (Paredes, 2008). Such graphene/solution dispersion has been used to fabricate the homogenous graphene oxide/polymer composites at a very low filler loading (~ 0.0375 wt%) (Yang, 2009c). However, graphene oxide sheets still form agglomerates in the polymer matrix at relatively high loading due to π - π stacking, strong hydrogen bond and Van der Waals force (Wan, 2014b). Many protective agents have been presented for improving the dispersion/exfoliation of graphene oxide in solution or polymer (Bao, 2011; Cao, 2011b; Xue, 2012), such as isocyanates (Stankovich, 2006c), hexachlorocyclotriphosphazene and glycidol (Bao, 2011), silane coupling agent (Yang, 2009b; Zeng, 2013), octadecylamine (Li, 2011b; Nawaz, 2012), block copolymer (Cao, 2011b), PVA (Cano, 2013; Cheng, 2012), poly(methyl methacrylate) (PMMA) (Gonçalves, 2010; Li, 2012e), and bio-based polyester (Tang, 2012). Recently, we used three types of organic molecules with different functional ended-groups including polyetheramine (PEA), 3-glycidoxypropyltrimethoxy (GPTMS) silane and diglycidyl ether of bisphenol-A (DGEBA) epoxy to modify graphene oxide sheets (Figure 7.5a) (Guan, 2014; Wan, 2014a; Wan, 2014b). The results revealed that the organic molecules attached to the sheets play a crucial role in determining the dispersion/exfoliation in the polymer composites (Figure 7.5b). Among the studied methods, the covalent functionalization of graphene oxide with DGEBA epoxy chains is promising for an epoxy composite system, since the grafted polymer chains can mix easily with the corresponding polymer matrix to lead to an improved dispersion and interface (Cheng, 2012; Deng, 2011; Lin, 2011; Liu, 2011; Salavagione, 2009), providing a convenient method to achieve the ideal reinforcing effect in polymer composites.

As above-mentioned, graphene oxide sheet is electrically insulating, limiting its application for conductive polymer composites. Normally, the electrical conductivity of graphene oxide can be significantly increased by reduction through removing the oxygen groups and re-hybridizing the effected sp^3 C atoms to sp^2 C. However, chemical reduction of graphene oxide in water and thermal reduction at high temperature of graphene oxide or GO sheets usually result in their irreversible restacking, which then makes dispersion of individual sheets in a polymer matrix difficult. For this reason, the residual oxygen groups of RGO sheets after the reduction can be functionalized to fabricate derivatives (Chen, 2012c; Fang, 2009, 2010a; Fang, 2010b; Guo, 2011c; Hsiao, 2010; Kerscher, 2013; Lu, 2012a; Ma, 2012; Ma, 2013a; Nethravathi and Rajamathi, 2008; Rafiq, 2010; Ramanathan, 2008; Tang, 2011b; Verdejo, 2008), showing promising to improve the compatibility of RGO sheets in a polymeric matrix. The surface covalent functionalization is usually effective to manipulate the physical and chemical properties of graphene sheets, as well as to facilitate the interfacial stress transfer from polymer to sheet (Guan, 2014). In particular, considering the rich chemistry of hydroxyl, carboxyl, and epoxy groups, GO has been selected very often as the starting material for the formation of graphene derivatives through the covalent attachment of organic groups on its surface (Georgakilas, 2012a). For example, based on mussel-inspired surface chemistry (Lee, 2007), dopamine molecules with adhesive property, reducing ability, high thermal stability, and high carbon-yielding characteristic were

used to surface functionalize graphene oxide (Kaminska, 2012; Kang, 2011; Lee, 2013b; Xu, 2010b). Since dopamine can serve as an effective reducing agent due to its oxidative self-polymerization to produce polydopamine, simultaneous reduction and surface functionalization of graphene oxide were thus obtained. Similar simultaneous reduction and functionalization of graphene oxide were also obtained by using different diamine molecules, such as octadecylamine (Li, 2011b), ethylenediamine (Kim, 2013) and polyetheramine (Tang, 2014a).

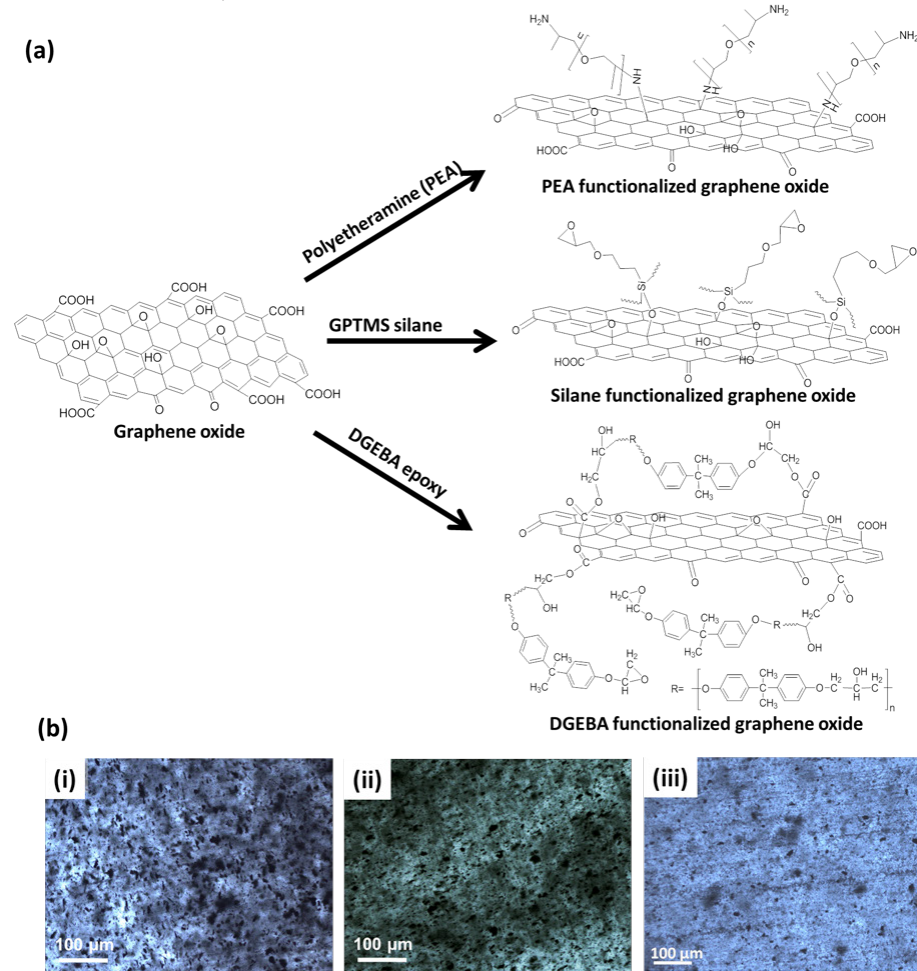


Figure 7.5. Covalent functionalization of graphene oxide for polymer composites: (a) schematic of synthesis of graphene oxide sheets functionalized by various organic molecules with different functional ended-groups (Guan, 2014; Wan, 2014a; Wan, 2014b) and (b) the optical images of sheet dispersion in epoxy resin: (i) 0.5 wt% graphene oxide, showing some clusters (dark dots) at a relatively high filler content, (ii) 0.5 wt% PEA functionalized graphene oxide (Guan, 2014), indicating the almost unchanged dispersion after the PEA functionalization and (iii) 0.5 wt% DGEBA functionalized graphene oxide (Wan, 2014b), demonstrating good dispersion due to the compatibility and miscibility between the functionalized graphene oxide and the epoxy matrix.

Herein, we briefly introduced the surface modification of graphene for fabricating polymer composites. More information about achieving a well-dispersed system by either covalent or non-covalent functionalization of graphene surface is referred to reviews on graphene chemistry (Dreyer, 2010; Georgakilas, 2012a; Kuila, 2012; Park, 2009).

7.3.3 Mechanical methods for dispersing graphene into polymer

Several main methods including ultrasonication, three roll mill, ball mill, stir and extrusion (Figure 7.6), have been widely used to disperse graphene and its derivatives into polymers, which is similarly to disperse CNT into polymers reported by Kim and co-workers (Ma, 2010).

Ultrasonication is the act of applying ultrasound energy to agitate nanofillers in a solution and/or polymer. The principle of this technique is that when ultrasound propagates via a series of compression, attenuated waves are induced in the molecules of the medium through which it passes (Ma, 2010). Such shock waves promote the “peeling off” of individual nanoparticles located at the outer part of the nanoparticle bundles, or agglomerates, and thus produce the separation of individualized nanoparticles from the agglomerates (Figure 7.6a). This method is an effective method to disperse and exfoliate graphene and obtain stable suspensions in various solvents with a low viscosity, such as water, acetone and ethanol (Luo, 2011; Paredes, 2008; Wajid, 2012). Considering the solid or viscous liquid nature of most polymers, they are usually required to be dissolved or diluted using a solvent to reduce the viscosity before using this method. It should be noted that both of frequency of ultrasound (most commonly used zone: 10-50 KHz) and treatment time are crucial parameters for the integrity of graphene structure and its dispersion state in polymer (Li, 2013d). In particular, ultrasonication can be used to tune the structure of graphene oxide sheets (Qi, 2013), and the sheets were exfoliated gradually in an appropriate time and further treatment led to a reverse trend. It was also found that the size of graphene oxide decreased sharply in the first hour and then remained almost unchanged with the extension of sonication, but such localized damage to graphene oxide deteriorated both of the electrical and mechanical properties of polymer composites.

Calender (e.g. three-roll or two-roll mill), is especially suits for elastomer and adhesive processing. The two or three roll mill methods employ the shear force created by rollers to mix, disperse or homogenize viscous materials. For instance, three-roll mill consists of three adjacent cylindrical rolls where three rolls turned at the different angular velocity ratio ($\omega_1 < \omega_2$, Figure 7.6b). The first and third rolls rotated in the same direction while the center roll rotated oppositely. Adjusting the gap distance (δg) and nip force between rolls resulted in high shearing stress, which could break up the nanoparticle agglomerates and hence generate highly dispersed polymer dispersion (Thostenson, 2006). A serial of polymer composites with low

loading of RGO sheets have been prepared by using the calendaring process (Ahmadi-Moghadam, 2014; Araby, 2013; Chandrasekaran, 2014; Hernández, 2012; Mannov, 2013; Potts, 2013; Prolongo, 2013), which is effective to improve the mechanical, thermal and electrical properties. Although some sheet clusters were still found in polymer (Chandrasekaran, 2014), the dispersion state can be tuned by changing the gap between the adjacent rolls (Ahmadi-Moghadam and Taheri, 2014).

Ball milling is a typical grinding method used to grind materials into extremely fine powder for use in paints, pyrotechnics and ceramics. During the milling, a high pressure is generated locally due to the collision between the tiny, rigid balls in a concealed container (Figure 7.6c), which can grind nanoparticle clusters to as small as nano-scale (below 100 nm) in polymer matrix, even exfoliate the graphite to be graphene sheets (Leon, 2011; Zhao, 2010a). Some useful functional groups can be successfully grafted onto graphene surfaces by using the ball milling process (Chen, 2013a; Wu, 2011). In general, ball milling processing can produce good graphene dispersion in polymer matrix, even further exfoliate the graphene sheets (Tang, 2013a). A one-pot method which involves peeling graphite sheets off into graphene and in situ producing graphene-based nanocomposites by ball milling has been presented in some works (Wu, 2011; Wu, 2012c). However, it is worthy to note that an appropriate milling time is very important since a relatively long balling time may significantly destroy the structure of graphene sheet and decrease the sheet size.

Stir is a common technique to disperse particles in liquid systems and can be also used to disperse graphene in a polymer matrix. Size and shape of the propeller and the mixing speed are important to determine the dispersion state of fillers in polymer. For dispersing nanofillers including alumina, CNT and graphene, higher shear speed (>2000 rpm) are needed to produce high shear round the stress around the propeller (Figure 7.6d) (Gao, 2014; Tang, 2013b; Tang, 2011a; Zhang, 2010a). After intensive stirring of graphene sheets in polymer matrix, although a relatively good dispersion and exfoliation state of sheet can be achieved, the dispersing effect by such method is still inferior to that by using the calendaring methods (Prolongo, 2013). Similarly, extrusion is a frequently used to disperse graphene into solid polymers like most thermoplastics. Twin screws in extruder hopper rotate at a high speed generating high shear flow through adjusting various parameters such as screw speed, temperature and time (Figure 7.6e), and it leads to graphene dispersing and mixed with polymer matrix. The extrusion method meets large-scale production of polymer composites, which has been used for fabricating high-performance graphene/polymer composites (Chatterjee, 2011a; Kalaitzidou, 2007; Steurer, 2009; Vallés, 2013; Zhang, 2010b). A drawback of this technique is that it may cause graphene buckling and even rolling or shortening due to the strong shear forces, thus reducing their aspect ratios, which is not favorable for achieving a low percolation threshold and high conductivity of the composites (Kim, 2010b).

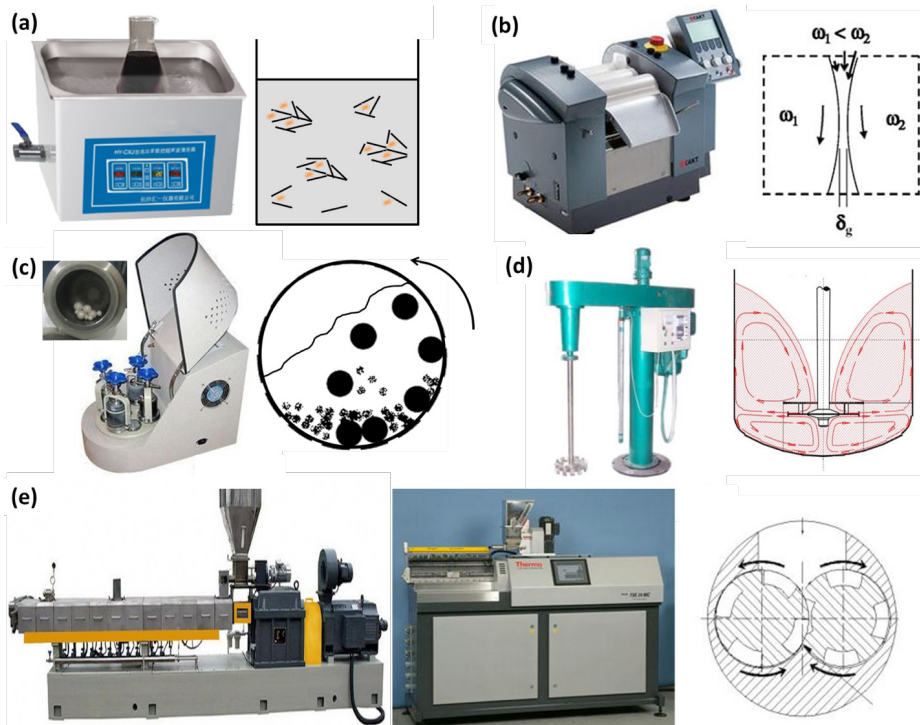


Figure 7.6. Mechanical methods and schematic of the related mechanisms for dispersing graphene into polymers: (a) ultrasonication, (b) calender, (c) ball milling, (d) high speed shear mixer and (e) extruder.

7.3.4 Fabrication of graphene/polymer composites

In order to facilitate industrial fabrication and application, directly using graphene as fillers to prepare polymer composites is preferred. Based on the above mechanical dispersing methods, there are three main strategies to achieve this: solution mixing, in situ polymerization and melt blending.

7.3.4.1 Solution mixing

Solution mixing is the most widely used technique for preparing graphene/polymer composites because it is amenable to small sample sizes and possesses a low viscosity condition for nanofiller dispersing. Typically, solution mixing method involves three major steps: dispersing graphene in a suitable solvent by mechanical mixing, magnetic agitation or sonication, then, mixing the nanofiller suspension with a polymer in the same solvent or in a mixed solvent by simple stirring or shear mixing, finally obtaining composite by removal of solvent through precipitating using a non-solvent for the polymer or directly evaporating solvent. This method is considered

an effective means to prepare composites with uniformly dispersed graphene or its derivatives. Many composites based on epoxy (Tang, 2013a; Teng, 2011; Wan, 2013; Yousefi, 2013b), PS (Stankovich, 2006a; Tang, 2014b), PMMA (Gonçalves, 2010; Li, 2012e), polyvinylidene fluoride (PVDF) (Shang, 2013), polypropylene (PP) (Yun, 2011), polyurethane (PU) (Chen and Lu, 2012c; Kim, 2010b; Yousefi, 2013a), etc., have been fabricated using this technique. However, it is worthy to note that solvent removal is a critical issue and the trace of the solvents always remains such as absorbed on the graphene even after careful removal and drying processes.

7.3.4.2 In situ polymerization

In situ polymerization is another very efficient method to obtain uniform dispersion of graphene and provide strong interaction between the graphene and polymer matrix. In this technique, the sheets are mixed with the monomers or pre-polymers, sometimes in the presence of a solvent, and then the polymerization occurs by adjusting condition such as temperature and time. Successful examples of in situ polymerization include PS (Liu, 2011), polyimide (PI) (Wang, 2011b), PP (Huang, 2010b), PU (Kim, 2010b; Li, 2013c), polyacrylonitrile (Yin, 2012), PS (Liu, 2011), PMMA (Potts, 2011b), epoxy (Guo, 2011c), phenol formaldehyde (Zhao, 2014). This technique is particularly important for the composites with insoluble or thermally unstable polymer matrices, which cannot be processed in solution or melt processing. However, the polymerization process is usually accompanied by an influence of the matrix polymerization and an increasing viscosity hinders manipulation and limits load stress (Verdejo, 2011). In addition, in some cases, this technique is carried out in the presence of solvents, and thus has the similar shortcomings as solution processing (Du and Cheng, 2012).

7.3.4.3 Melt blending

Melt blending is much more economical and scalable than both solvent mixing and in situ polymerization. This technique utilizes both high-shear forces and high temperature melting to blend the filler and matrix materials, so it is more environmentally friendly than solvent mixing. However, because of thermal instability of most chemically modified graphene, use of melt blending for graphene has so far been limited to a few studies with the thermally stable graphene. Thermoplastic polymers, such as PU (Kim, 2010b), PS (Shen, 2011; Zhang, 2010b), polycarbonate (PC) (Shen, 2013b), PP (Hsiao, 2011), PA (Yuan, 2013), poly(styrene-co-acrylonitrile) (Steurer, 2009), polyurethane 12 (PA12) (Yan, 2012), and elastomers (Araby, 2013), can be processed as matrix materials by using this processing. The shortcomings of this procedure are the low bulk density of thermally exfoliated graphene that makes extruder feeding to be a troublesome task and the low degree dispersion of filler. Meanwhile, the high shear forces employed can sometimes cause the breakage of graphene sheets. These drawbacks are detrimental to the performances of composite,

so optimization of melting process for high performance polymer composites is a challenging but significant task.

The fabricating processes play crucial roles in determining the dispersion and exfoliation of graphene and its derivatives in polymers and thus influencing the final performance of graphene/polymer composites. Several works have compared the effect of different processing methods through characterization of filler dispersion and performance of composite (Kim, 2010b; Potts, 2013; Raza, 2012; Tang, 2013a). For example, Macosko and co-workers prepared PU based composites containing thermally reduced GO (TRG) by using three different methods of dispersion: solvent blending, in situ polymerization, and melt compounding (Kim, 2010b). The results revealed that the structure and performance of the composites are closely related to preparing methods and can be tailored by experiencing a certain processing procedure. It was found that solvent processed composites have higher stiffness and lower electrical percolation threshold than melt mixing processed composites. This observation is in good qualitative agreement with the dispersion level inferred from solid property enhancements (Figure 7.7a).

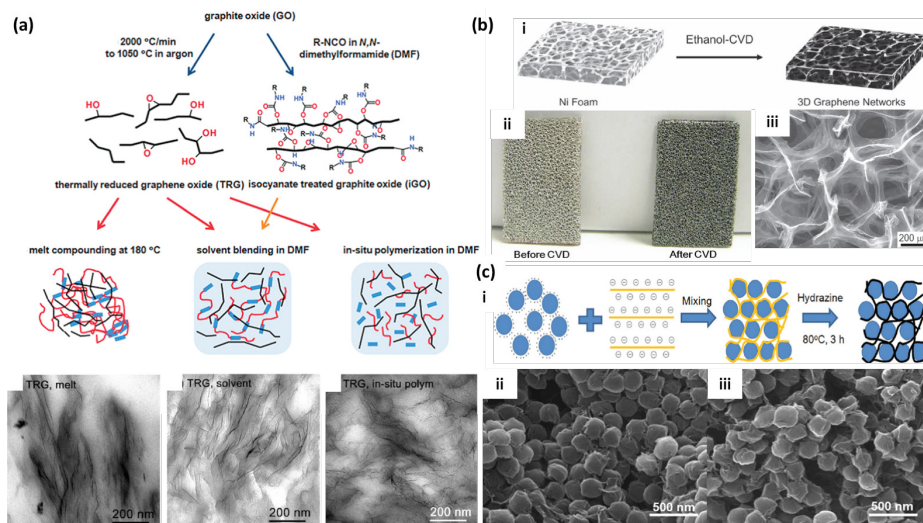


Figure 7.7. Various fabricating processes for fabricating graphene/polymer composites: (a) schematics of TRG/TPU composite preparation routes and their TEM images of TRG in TPU and TEM images of 3.0 wt% TRG/PU composites prepared different fabricating processes, showing the better dispersion/exfoliation of TRG obtained by the solution mixing and in situ polymerization compared to melt blending (Kim, 2010b); (b) porous graphene scaffolds synthesized by the ethanol-CVD method (Cao, 2011a): (i) schematic illustration of the synthesis of 3D graphene networks on Ni foam by ethanol-CVD, (ii) photographs of Ni foam before and after the growth of graphene and (iii) 3D graphene networks after removal of Ni foam; (c) 3-D RGO network via a self-assembly process (Pham, 2012): (i) schematic illustration of self-assembly of PMMA latex and graphene oxide, followed by hydrazine reduction of graphene oxide, and SEM images of RGO/PMMA composites filled with different filler loading: (ii) 2.0 wt% and (iii) 4.0 wt%.

7.3.4.4 Other methods

Recently, some novel methods have been developed to synthesize graphene/polymer composite materials with 3-D porous graphene scaffolds (Cao, 2011a; Chen, 2011; Jia, 2014; Li, 2014a; Pham, 2012; Vickery, 2009; Wu, 2013a; Wu, 2013b). Typically, CVD, template and lyophilization methods have been used to prepare 3-D porous graphene scaffolds (Barg, 2014; Cao, 2014; Sun, 2013c) (Figs. 7b and 7c). In the CVD method, carbon was first introduced to the nickel foam by decomposing carbon sources such as hydrocarbon gases, and a graphene film with a continuous and interconnected 3-D network was then produced on the surface of the nickel foam (Cao, 2011a; Pettes, 2012). Then, the porous graphene scaffolds can be used to prepare high mechanical performance and conductive graphene/polymer composites (Chen, 2011; Jia, 2014). In the template approach, highly conductive polymer composites with 3-D graphene scaffolds can be prepared by a self-assembly of positively charged polymer latex particles and negatively charged graphene oxide sheets through electrostatic interactions, followed by hydrazine reduction (Choi, 2012b; Pham, 2012; Wu, 2013a). In the lyophilization method, the graphene or graphene oxide dispersion was frozen at a low temperature, and the solvent was converted to the solid state and removed by a drying process in vacuum. Gao and co-workers prepared the multifunctional, ultra-flyweight graphene/CNT aerogels by injecting aqueous dispersion of graphene oxide and CNT into liquid nitrogen during the lyophilization, followed by the chemical reduction of hydrazine vapor (Sun, 2013b). Liao and co-workers synthesized graphene sponge scaffold from graphene oxide solution by a hydrothermal method combined with freeze drying and then infiltrated epoxy into such porous graphene structure to prepare highly conductive composite materials (Li, 2014a).

7.4 Properties of graphene/polymer composites

7.4.1 Mechanical properties

The in-plane elastic modulus and fracture strength of defect-free graphene are ~ 1.0 TPa and ~ 130 GPa (Lee, 2008), respectively. Despite some structural distortion, the measured elastic modulus of RGO sheets is still as high as 0.25 TPa through tip-induced deformation experiments (Gómez-Navarro, 2008). As a comparison, Figure 7.8a presents a chart of Young's modulus as a function of density comparing graphene properties to more traditional materials (Verdejo, 2011), indicating that the defect-free graphene is the stiffest and strongest material ever reported in nature. These outstanding intrinsic properties of graphene or RGO sheets (compared to most polymeric materials), coupled with their large surface areas, allow them to be the primary load-bearing component of polymer composites. Therefore, graphene-filled-polymer composites has attracted a great deal of attentions and become one of the most explored directions in composite materials now (Sun, 2013c).

The mechanical properties can be significantly improved by incorporating graphene into polymers, even showing advantages of graphene in mechanical reinforcement over existing carbon fillers such as carbon black (CB), expanded graphite (EG), and single-walled carbon nanotubes (SWNT) (Rafiee, 2010; Rafiee, 2009; Ramanathan, 2008; Shadlou, 2013; Steurer, 2009; Tang, 2014b; Wang, 2011d; Yavari, 2010; Zandiatashbar, 2012). Zhao et al. had developed a fully exfoliated RGO/PVA composite by an aqueous solution mixing method (Zhao, 2010b). Compared with the pure PVA polymer, the tensile strength and Young's modulus had been increased by 150% and appropriately ten times at 1.8 vol% of RGO, respectively (Figure 7.8b). Ramanathan et al. investigated and compared thermal and mechanical properties of PMMA-based composite containing functionalized graphene sheets (FGS), SWNTs and EG fillers (Figure 7.8c) (Ramanathan, 2008); and the results suggest that the presence of the wrinkles may actually lead to nanoscale surface roughness which likely produce an enhanced mechanical interlocking and adhesion with the polymer chains. Also, comparative studies of both RGO and CNT filled polymer composites made by Rafiee et al. (Rafiee, 2009; Yavari, 2010) revealed greater improvements for RGO/polymer than for CNT/polymer systems (Figure 7.8d). Recently, we also investigated the creep and recovery of PS composites with different geometrical morphologies of carbon nano-additives i.e CB, multi-wall carbon nanotube (MWCNT) and CRGO sheets (Tang, 2014b). At a fixed loading of fillers, the CRGO sheets showed better efficiencies in reducing the creep and unrecovered response than the CB and MWCNT fillers (Figure 7.8e).

When dispersed in a polymer matrix, these compliant RGO sheets usually show wrinkled structures which may effectively reduce these modulus values (Tang, 2013a), as crumpled sheets would tend to unfold rather than stretch in-plane under an applied tensile stress. This nanoscale surface roughness likely leads to increased mechanical interlocking with polymer chains and consequently strengthens the interaction and load transfer between graphene and the polymer matrix. Thus, the reinforcing/toughening effectiveness observed from these materials thus far may be limited by problems with dispersion and exfoliation of sheets in the polymer matrix. The restacking and/or incomplete exfoliation of RGO sheets could lead to lower effective modulus values due to the decreased aspect ratios; and the weak van der Waals forces exist between individual shells of the graphene agglomerates (Chen and Lu, 2012c), slipping between the shells will occur. It has been suggested that such aggregates may be highly compliant and could reduce the effective aspect ratio of the filler, with both factors diminishing the reinforcing/toughening effect (Schaefer, 2007). Previous work demonstrated that epoxy composites with highly dispersed RGO showed higher tensile strength and fracture toughness than those with poorly dispersed RGO (Figs. 9a and 9b) (Tang, 2013a), and the sheets were observed to debond/delaminate and bridge the micro-crack during fracture process due to the poor filler/matrix and filler/filler interfacial quality (Figs. 9c and 9d), which should be the key elements of the reinforcing and toughening effects on epoxy resin.

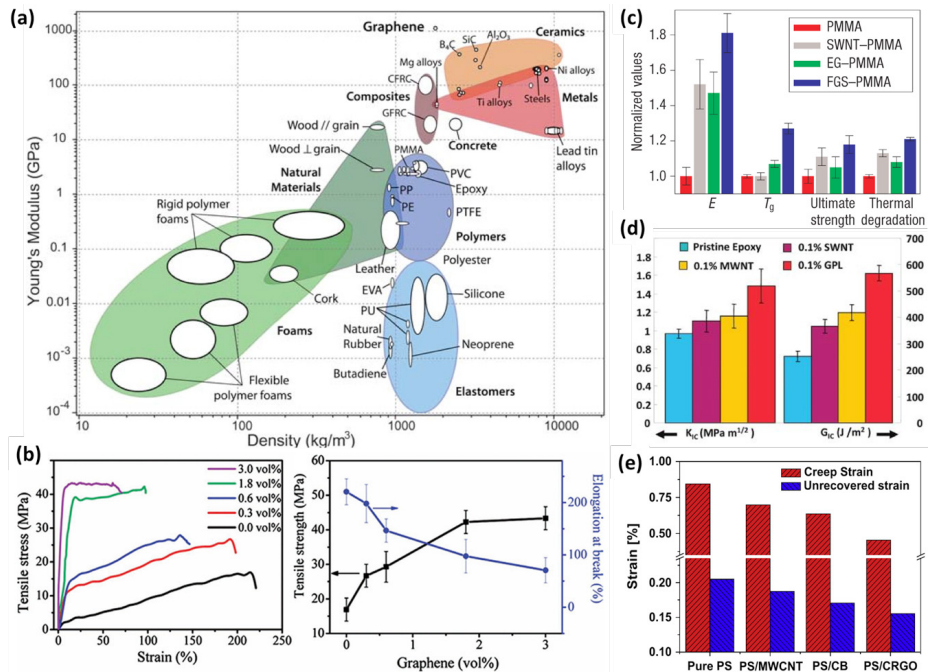


Figure 7.8. Mechanical properties of graphene and graphene-reinforced-polymer composites: (a) chart of Young's modulus as a function of density comparing graphene properties to traditional materials (graphene density was taken as 2200 kg/m^3) (Verdejo, 2011); (b) tensile properties of graphene/PVA composites: typical stress-strain curves (left) and dependence of the tensile strength and elongation (right) on the graphene volume concentration (Zhao, 2010b); (c) summary of mechanical and thermal property improvements for PMMA composites containing 1 wt% FGS, SWNT and EG fillers (Ramanathan, 2008) (All property values are normalized to the values for neat PMMA; neat PMMA values are Young's modulus, $E=2.1 \text{ GPa}$, $T_g=105 \text{ }^\circ\text{C}$, ultimate strength= 70 MPa , thermal degradation temperature= $285 \text{ }^\circ\text{C}$); (d) fracture toughness (K_{IC}) and fracture energy (G_{IC}) for the baseline epoxy and GPL/epoxy, MWNT/epoxy, and SWNT/epoxy nanocomposites at $\sim 0.1 \text{ wt}\%$ fraction of nanofillers (Rafiee, 2009); (e) creep strain and unrecovered strain at 900s of pure PS and its composites with 5.0 wt% MWCNT, CB and CRGO fillers under the applied stress of 8 MPa and environment temperature of $60 \text{ }^\circ\text{C}$ (Tang, 2014b).

As is well known, the mechanical properties of polymer composites are not only determined by the dispersion levels of nanofillers, but are also essentially dependent on their interface with the polymer host (Huang, 2012a; Shim, 2012; Verdejo, 2011; Yousefi, 2013a; Zaman, 2011). A strong interfacial bond between the RGO sheet and the surrounding polymer matrix is crucial to determine the mechanical performance of polymer composites (Kim, 2010b; Liang, 2009a; Paul, 2008; Shen, 2013a; Wang, 2011f). In the composites, incompatibility between the phases may lower stress transfer due to poor interfacial adhesion, resulting in a lower modulus (Schadler, 1998). Gong et al. measured the graphene/polymer interfacial adhesion by using Raman spectroscopy

measured under strain (Gong, 2010). The results revealed an interfacial shear stress of ~2.3 MPa in a graphene/PMMA composite (where graphene was produced by micro-mechanical exfoliation), suggesting that the interaction between PMMA and the monolayer graphene was relatively weak. Previous work has also demonstrated that the mechanical properties of the polymer composites are slightly improved after the presence of pristine graphene, but not enough as expected (Rafiee, 2009; Wang, 2012c; Zaman, 2012a), especially for the elastic modulus. As the above-mentioned discussion, surface modification of the surface or edges of RGO and its derivatives is effective to significantly improve the graphene/polymer interface through covalent and non-covalent bonding (Das, 2012b; Fang, 2010b; Hu, 2014; Layek, 2012; Meng, 2014; Naebe, 2014; Park, 2013b; Potts, 2011b; Shen, 2013b; Tang, 2011b). For example, the non-ionic surfactant treatments of Triton X-100 were effective to improve the dispersion and interface in the RGO/epoxy composites (Wan, 2013); and the debonding between the untreated RGO and the matrix seems to be restricted after the surfactant treatment (Triton-RGO) as indicated by the black arrows in Figure 7.9e. As a result, the tensile strength and fracture toughness of the composites were thus greatly improved. Aside from the main issues of the dispersion and interface, the mechanical performance of graphene/polymer composites are strongly influenced by other several factors, such as intrinsic structure, size and properties of RGO sheets as well as orientation in polymer (Chatterjee, 2012; Du and Cheng, 2012; Layek, 2012), which is still further investigated to optimize the mechanical properties of the composites.

In general, graphene oxide sheets are also attractive fillers for reinforcing/toughening polymer (Vallés, 2013; Wan, 2012; Wang, 2013b), which is due to the following reasons: (i) it has excellent mechanical properties, such as elastic modulus of ~207.6 GPa (Suk, 2010); (ii) it has abundant functional groups, which facilitate strong interfacial interaction and load transfer from the host polymers to the sheets (Wang, 2011e; Yang, 2009c); (iii) the functional groups can significantly alter the van der Waals interactions between the sheets, making them easier to disperse in polymer matrices (Liang, 2009a). For example, Bortz et al. found 28-111% enhancements in mode I fracture toughness (*K_{IC}*) and up to 1580% in uniaxial tensile fatigue life through the addition of small amounts (<1.0 wt %) of graphene oxide to an epoxy system (Bortz, 2012). Compared to the traditional and natural 2-D fillers of clay, graphene oxide has a weight and flexibility advantage, so that polymer composites containing graphene oxide sheets are more applicable as structural materials requiring lightweight and/or flexibility. In order to further improve the mechanical performance of the graphene oxide/polymer composites, chemical modification is an effective method of manipulating the physical and chemical properties of graphene oxide to improve the interfacial interaction with a polymer matrix (Nawaz, 2012; Satti, 2010; Yun, 2011), especially the grafted polymer chains for the corresponding polymer composites (Fang, 2009; Gonçalves, 2010; Liu, 2011; Shen, 2013a). For example, in epoxy system, the DEGBA epoxy functionalization of graphene oxide (DGEBA-f-GO) improved the dispersion of graphene oxide and its interfacial interactions with the

epoxy matrix (Wan, 2014b); and consequently, the elastic modulus (+13%), strength (+75%) and fracture toughness (+41%) of epoxy were simultaneously and significantly enhanced at a DGEBA-f-GO loading of 0.1 wt%. When compared with those of other epoxy systems with similar GO weight content (0.10-0.50 wt%) (Bortz, 2012; Chen, 2012a; Jiang, 2013; Li, 2013e; Wang, 2013b; Yousefi, 2013b), the DGEBA-f-GO/epoxy samples exhibited a good balance among the thermal properties, tensile strength and elastic modulus as well as fracture toughness.

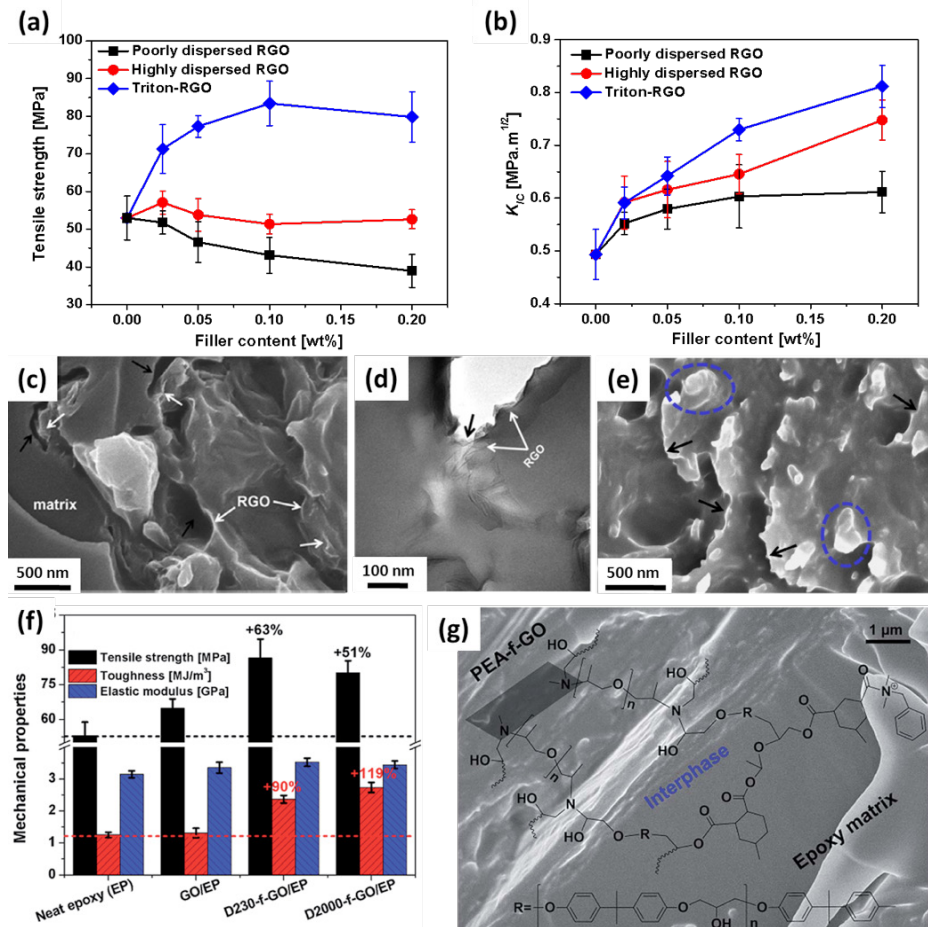


Figure 7.9. Mechanical properties of polymer composites as a function of different dispersion and interface conditions: (a) tensile strength and (b) fracture toughness of epoxy composites filled with poorly and highly dispersed RGO and surfactant-treated RGO (Tang, 2013a; Wan, 2013); (d) SEM and (e) TEM image of the composite filled with untreated RGO, showing the sheet/matrix debonding and graphene bridging a propagating micro-crack; (f) SEM image of epoxy composites containing Triton-RGO. (f) Mechanical properties of epoxy composites with different chain lengths of polyetheramine (PEA, D230 and D2000) functionalized graphene oxide and (g) the proposed PEA-functionalized-GO/epoxy composite formation mechanism (Zang, 2015).

Interface design also plays a crucial role in developing superior mechanical performance of graphene oxide/polymer nanocomposites. Recently, we used two types of PEA molecules with different molecular lengths (D230 and D2000) to synthesize the PEA-f-GO sheets (Guan, 2014). The addition of PEA-f-GO was found to produce significant enhancements in the mechanical properties of epoxy, including elastic modulus, tensile strength, elongation at break and toughness. In particular, the PEA-f-GO sheets containing shorter PEA molecules produced higher improvement in strength but smaller increases in both ductility and toughness than those containing longer PEA molecules. For example, at 0.50 wt% filler loading, the two composites showed ~63% and 51% increases in tensile strength and 90% and 119% in toughness as compared to the unfilled epoxy (Figure 7.9f). The results indicated that the effective and tunable interphases between the polymer host and the graphene oxide sheets (Figure 7.9g), established by varying the molecular lengths of grafted modifiers, not only promote load transfer but also modulate the structure of organic networks such that the strength and toughness of composites can be optimized simultaneously.

7.4.2 Electrical conductivity

Conductive fillers are generally employed to insulating polymer matrices to realize electrical conductivity. This can be explained by a percolation theory, i.e., conductive fillers form conductive pathways, i.e. percolation thresholds after they reach a critical concentration with an onset of conductivity (Bauhofer, 2009). Once electrical percolation has been achieved, the increase in conductivity as a function of filler loading can be modeled by a simple power-law expression: $\sigma_c = \sigma_f [(\Phi - \Phi_c) / (1 - \Phi_c)]^t$, where σ_f is the conductivity of the filler, Φ the filler volume fraction, Φ_c the percolation threshold (the onset of the transition), and t is the ‘universal critical exponent’. The large aspect ratio and high electrical conductivity of graphene and its derivatives make it promising conductive fillers to improve the electrical properties of various polymers, including PMMA (Li, 2012e; Pham, 2012; Zhang, 2012a), PVA (Das, 2012b; Zhou, 2011), poly(vinyl chloride) (PVC) (Vadukumpully, 2011), polyethylene terephthalate (PET) (Zhang, 2010b), PP (Huang, 2010b), polyethylene (PE) (Pang, 2010), PU (Kim, 2010b; Liao, 2012), polyamide (PA12) (Chatterjee, 2011b; Yan, 2012), PS (Li, 2011b; Ma, 2012; Pham, 2011; Qi, 2011; Stankovich, 2006a; Wu, 2012d), epoxy (Jia, 2014; Luan, 2012; Meng, 2014; Monti, 2013; Yang, 2012a; Zaman, 2012a; Zaman, 2012b). Stankovich et al. investigated the electrical conductivity of RGO/PS composites as a function of filler volume fraction (Figure 7.10a) (Stankovich, 2006a); and the results revealed that the RGO/PS composites exhibit a typical percolation behavior (percolation value: near 0.1 vol%) and the introduction of RGO to PS can increase the conductivity to higher than 10 orders of magnitude. The composites containing only ~1.0 vol% RGO loading show crumpling, wrinkling and folding morphologies (Figure 7.10b) and have an electrical conductivity value of ~0.1 S/m, indicating that highly conductive graphene/polymer composites can be constructed using a low loading of graphene.

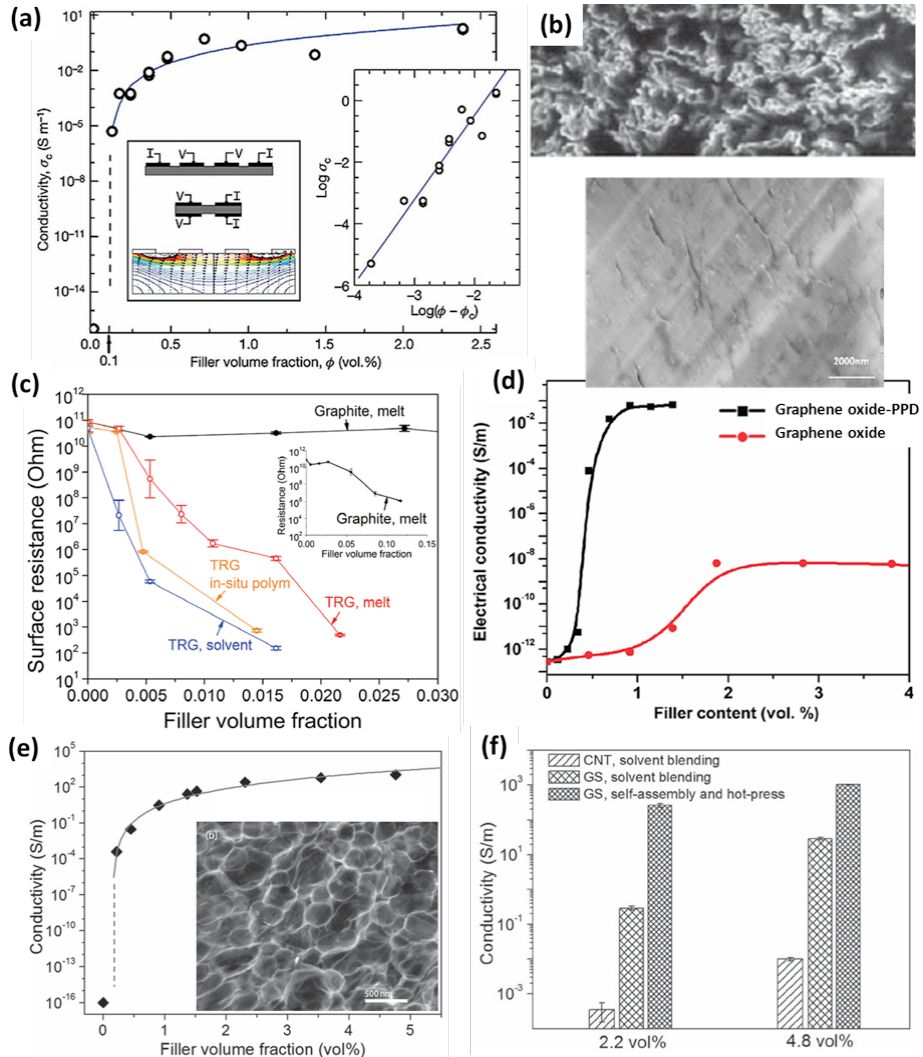


Figure 7.10. Electrical properties of polymer composites prepared by using different fabricating processes: (a) electrical conductivity of PS composites filled with isocyanate-functionalized RGO prepared by the solution blending method (top, the fitting curves of the experimental data to the effective conductivity equation) and (b) the microtomed composites with ~1.0 vol% RGO sheets, revealing the crumpling, wrinkling and folding morphologies of sheets (Stankovich, 2006a); (c) surface resistance of melt-blended graphite/PU composites (closed symbols, also in inset) and melt-blended, solution-mixed, and in situ polymerized TRGO/PU composites (Kim, 2010b); (d) Electrical conductivity of PS composites filled with graphene oxide and PPD functionalized graphene oxide by using solution blending (top: TEM images of PS composites containing 3.0 wt% graphene oxide-PPD) (Ma, 2012); (e) conductivity of graphene/PS composites as a function of filler volume fraction prepared by electrostatic self-assembly method (percolation value: 0.15 vol%; inset: SEM images of remained graphene skeleton after annealing the testing samples) and (f) electrical conductivity comparison of graphene and CNT-PS composites fabricated by the solution mixing and electrostatic self-assembly methods (Wu, 2013a).

An outstanding electrically conductive graphene/polymer composite is expected to have lower Φ_c and higher conductivity at a lower filler loading, which can not only decrease the cost of filler loading but also preserve the processability of the composite. A theoretical study by Xie et al. predicted that graphene is more effective for conductivity improvement than corresponding CNTs because of their large specific surface area (Xie, 2008). However, experimental comparison of electrical conductivity and percolation thresholds between graphene- and CNT-based polymer composites show complicated. Comprehensive data compiled on CNT-based polymer composites reveals that the CNT/epoxy composites have been reported with electrical percolation thresholds as low as approximately 0.0025 wt% (Bauhofer and Kovacs, 2009; Martin, 2004), which is usually far lower than those for graphene-based polymer composite (Das, 2012a). This discrepancy may be attributed to the following reasons reported by Du et al. (Du and Cheng, 2012): (i) graphene is easier to aggregate than MWCNTs in some cases due to its larger surface area and restacking; (ii) TRGO is apt to wrinkle and crimp, thus resulting in a lower aspect ratio; (iii) 2-D graphene is more difficult to interlace each other into a network structure than 1-D CNTs.

The electrical percolation threshold of graphene/polymer composites depends on the dispersion, alignment, intrinsic properties of the graphene sheets as well as their network structures in the polymer matrix. The effective fabrication methods are essential to disperse graphene, keeping them flat and preventing them from restacking and rolling, thus producing an effective conductive network. Kim et al. investigated the electrical properties of TRG/PU composites fabricated by three different methods of dispersion: solvent blending, in situ polymerization, and melt compounding (Kim, 2010b). The results showed the composites prepared by solution blending have the highest electrical conductivity and lowest percolation value among three systems (see Figure 7.10c), which is strongly dependent on the dispersion state of TRG in the matrix. On the other hand, although the dispersion states were similar for both solvent and in situ polymerization methods, the electrical conductivity of the two composite systems showed different. The differences among solvent and in situ polymerization could arise from the intimate contact between the graphene sheet and the polymer chains attained by in situ polymerization which effectively coats the sheet and shields it from the others (Verdejo, 2011). As reported in Ref. (Schaefer and Justice, 2007), it has been said that a high degree of dispersion may not necessarily yield the lowest onset of electrical percolation because a sheath of polymer may coat the surfaces of well-dispersed filler and prevent direct interparticle contact.

Another strategy to prepare conductive RGO/polymer composites is based on the starting materials of graphene oxide by the above-mentioned methods. Ma and his coworkers reduced and functionalized simultaneously graphene oxide by simple refluxing with p-phenylene diamine (PPD) in the presence of NH_3 solution. The functionalization of graphene oxide with PPD (graphene oxide-PPD) substantially

enlarged the interlayer spacing of graphene oxide sheets, which effectively prevented their aggregation after reduction (Figure 7.10d). Thus, graphene oxide-PPD was efficient in improving the electrical conductivity of PS, leading to a sharp conductivity transition with a low percolation threshold of ~ 0.34 vol%. Yousefi et al. prepared graphene oxide/waterborne epoxy composites using an easy, all aqueous, in situ polymerization method, and achieved highly stable RGO/epoxy dispersions, leading to the formation of composites with a self-aligned layered structure (Yousefi, 2013b). The highly aligned, ultralarge RGO sheets gave rise to a remarkable percolation threshold of 0.12 vol%. When the platelets are aligned in the polymer matrix, there are, at least at relatively low concentrations, fewer contacts between them, and thus the percolation threshold could be expected to increase.

Recently, construction of a 3-D, compactly interconnected graphene network is promising to prepare highly conductive polymer composites with low percolation threshold and high conductivity. Different from the graphene structures in polymer matrix formed by the conventional processing methods, the resulting 3-D porous graphene scaffolds would realize a uniform distribution of graphene without aggregation in polymer matrix and produce graphene sheets tightly contacting between them. Based on CVD of carbon occurred on nickel foams, Cheng and co-workers prepared flexible graphene/poly(dimethylsiloxane) composite films from the porous graphene scaffold with a high electrical conductivity of ~ 1000 S/m at a low graphene loading of ~ 0.5 wt% (Chen, 2011). Wu et al. used a self-assembly process to fabricate highly conductive PS nanocomposites with 3-D compactly interconnected graphene networks (Wu, 2013a) (Figure 7.10e), which is superior to that of the graphene- or CNT- based composite prepared by a solvent mixing method (Figure 7.10f). Similar 3-D scaffolds structures were established in other polymer composite systems (Chen, 2014; Li, 2014a; Ren, 2012), such as PVDF-based composites with a percolation value of ~ 0.105 vol% (Li, 2013b) and poly (methyl methacrylate-cobutyl acrylate) composites with a low percolation value of ~ 0.1 vol% (Noël, 2014). To the best of our knowledge, the lowest percolation threshold achieved thus far for a graphene-based polymer nanocomposite (~ 0.07 vol%) was observed when the filler was not homogeneously dispersed in the polymer matrix, but rather segregated from the matrix to form a conductive network (Pang, 2010).

7.4.3 Thermal conductivity

In addition to the excellent mechanical and electronic properties, graphene and its derivatives exhibit unusually high intrinsic thermal conductivity (Balandin, 2008; Cai, 2010b; Chen, 2012b; Ghosh, 2008), which has been measured to exceed 3000 W/mK when suspended (Balandin, 2008; Ghosh, 2008). The physics of phonons (the main heat carriers in graphene) has been shown to be substantially different in 2-D crystals, such as graphene, from three-dimensional 3-D graphite (Balandin,

2011; Ghosh, 2010). The 2-D geometry of graphene sheets may provide lower interfacial thermal resistance and thus produce highly-improved conductivity for polymer composites (Yu, 2008), even impart significant anisotropy to the thermal conductivity of the polymer composite (Kalaitzidou, 2007), due to the measured in-plane thermal conductivity as much as ten times higher than the cross-plane conductivity (Veca, 2009). Nevertheless, unlike the exponential increase in electrical conductivity, the thermal conductivity improvement produced by graphene fillers is not dramatic, although 2-D graphene can improve the thermal conductivity more effectively than 1-D CNT (Hu, 2010; Song, 2012a; Yu, 2007). This may be explained by the fact that the contrast in thermal conductivities between graphene and polymer is very smaller when compared to that in their electrical conductivities.

As is well known, thermal energy is transmitted by the interaction of adjacent particles through a combination of vibrations and free electrons. Interfacial thermal resistance across a filler/matrix or filler/filler interface is well known to limit the thermal conductivity of the composite (Zhong, 2006). Since phonons are the primary mode of thermal conduction in polymers, an effective interface between the matrix and filler can reduce phonon scattering at the matrix/filler interface, promoting higher thermal conductivity (Ganguli, 2008; Song, 2013). Hu and co-workers investigated the thermal conductivity of epoxy-based composites containing 4,4-diaminodiphenyl sulphone (DDS) functionalized graphene (D-graphene) and compared it with other carbon fillers including expandable GO (EGO), DDS functionalized EGO (D-EGO), pristine MWCNTs and DDS functionalized MWCNTs (D-MWCNTs). The results in Figure 7.11a revealed that DDS functionalization can obviously improve the interfacial heat transfer between the carbon materials and the epoxy matrix due to enhanced interfacial bonding (Hu, 2010). Similarly, Teng and co-workers synthesized the poly(glycidyl methacrylate) (PGMA) containing localized pyrene groups (Py-PGMA) to non-covalently functionalize graphene nanosheets (GNSs) through π - π stacking (Teng, 2011). The Py-PGMA on the GNS surface not only plays an important role to facilitate a homogeneous dispersion in the polymer matrix but also improves the GNS/polymer interaction. Consequently, the thermal conductivity of integrated Py-PGMA-GNS/epoxy composites exhibited a remarkable improvement and is much higher than epoxy reinforced by MWCNTs or GNSs (Figure 7.11b). The thermal conductivity (1.91 W/mK) of 4 phr PyPGMA-GNS/epoxy composites has ~20% (higher than that of pristine GNS/epoxy composites) and 267% (higher than pristine MWCNT/epoxy composites) improvements.

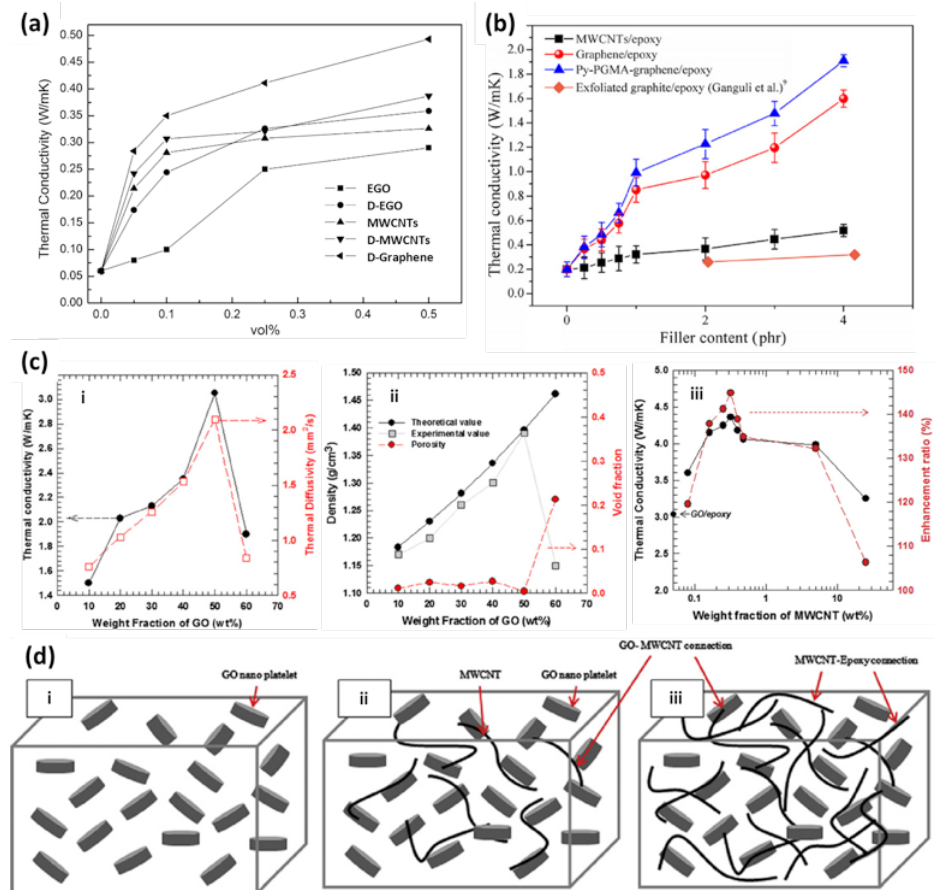


Figure 7.11. Thermal conductivity of graphene-based polymer composites: (a) thermal analysis of neat epoxy and composites with 0.1 vol% EGO, MWCNT and D-graphene (Hu, 2010); (b) influence of surface modification of graphene on thermal conductivity of epoxy composites and the comparison of thermal conductivity of epoxy composites filled with MWCNT and exfoliated graphite (Teng, 2011); (c) thermal conductivity of graphene oxide-CNT hybrid/epoxy composites (Im and Kim, 2012): (i) thermal transport properties and (ii) theoretical expected and experimental porosity of GO/epoxy composite and (iii) thermal conductivities of GO/MWCNT/epoxy composites as a function of the MWCNT loading, and (d) schematic diagrams of GO/MWCNT/epoxy composites (i) in the absence of MWCNTs, with a MWCNT loading of (ii) 0.36 wt% and (iii) 0.48 wt%.

Thermal conductivity of polymer composites containing graphene- or graphene nanoplatelet (GNP)- based hybrid fillers has attracted much interest (Chu, 2012; Im and Kim, 2012; Shahil, 2012a; Shahil, 2012b; Yu, 2008). Yu and co-workers found a synergistic effect of combining SWCNTs and GNPs on improving the thermal conductivity of epoxy (Yu, 2008). The epoxy composites with 10 wt% loading of the individual fillers gave thermal conductivities of $k_{\text{SWCNT}}=0.85$ W/mK for the SWNT filled composite and

$k_{\text{GNP}}=1.49$ W/mK for the GNP-filled composite; comparatively, the hybrid composites showed pronounced maximum thermal conductivities of $k_{\text{HYBRID}}=1.75$ W/mK at a ratio of approximately 3:1 of GNP:SWCNT, which is attributed to the SWCNTs bridged across adjacent GNP platelets, forming an extended network of filler in direct contact. As shown in Figure 7.11c, significant improvements in thermal conductivity have been achieved in these hybrid GO/MWCNT/epoxy systems (with composite conductivities ranging from 3 to 6 W/mK, up from approximately 0.2 W/mK for neat epoxy), but such large gains require relatively high carbon loadings (20 wt% and higher). When the total amount of fillers was fixed 50 wt% while changing the amount of MWCNTs, a maximum thermal conductivity was obtained with the addition of about 0.36 wt% of MWCNTs in the fillers. However, the thermal conductivity decreased for MWCNT concentrations above 0.4%. The increased thermal conductivity was due to the formation of 3-D heat conduction paths by the addition of MWCNTs (Figure 7.11d); whereas too high a MWCNT concentration led to increased phonon scattering, which in turn led to decreased thermal conductivity.

7.4.4 Thermal stability, glass transition temperature and dimensional stability

Due to the unique structure and high thermal stability, integration of graphene and its derivatives into polymer matrices can significantly improve their thermal stability and glass transition temperature. Thermal degradation temperature, characterized by the maximum weight loss rate in thermogravimetry, can be enhanced by 10-100 °C at a low filler loading (<10 wt%) for various polymers, such as epoxy (Prolongo, 2013; Shen, 2013a; Wan, 2014a; Wan, 2014b; Wan, 2013; Wang, 2012c), poly(lactic acid) (PLA) (Cao, 2010), PS (Cao, 2011b; Ma, 2012), PC (Xu, 2013a), PU (Cai, 2012), PE (Kuila, 2011), PP (Song, 2011; Yun, 2011), poly(butylene succinate) (PBS) (Wang, 2011c), PVA (Cheng, 2012; Guo, 2011b; Liang, 2009a; Xu, 2009), phenol formaldehyde (PF) (Zhao, 2014), PMMA (Gonçalves, 2010; Hu, 2014; Potts, 2011b; Ramanathan, 2008; Vallés, 2013; Wang, 2011f; Yang, 2012d), and silicone materials (Ma, 2013b; Verdejo, 2008). Decomposition of graphene based polymer composites is substantially slower than neat polymers, which is attributed to restricted chain mobility of polymers near the graphene surface. During combustion, inflammable anisotropic nanoparticles form a jammed network and “tortuous path” effect of char layers that delay the escape of volatile degradation products and also char formation (Cao, 2010; Huang, 2012a; Kashiwagi, 2005).

In general, the presence of well-dispersed graphene usually improves the T_g value of polymer significantly at a low filler loading (<5.0 wt%) (Beckert, 2012; Bora, 2013; Cheng, 2012; Fang, 2009; Liang, 2009a; Martin-Gallego, 2011; Naebe, 2014; Tang, 2013a; Wan and Chen, 2012; Wang, 2013b; Wang, 2011f; Yousefi, 2013b; Zaman, 2012b). Some previous work revealed that RGO sheets are much more effective to increase the T_g value of polymer matrix than the corresponding CNTs (Ramanathan, 2008; Zaman, 2012b),

which probably attributed to the following reasons: (i) for the polymer composites with pristine CNTs, localized clustering leads to nanotube-rich and nanotube-poor regions (Tang, 2011a), which makes the polymer molecules to move easily and thus decreased or remained the T_g s (Shen, 2007), and similar phenomenon was also observed in the composites with the poorly dispersed RGO and thus results in almost unchanged T_g value (Tang, 2013a); (ii) the nanotubes are curled up and thicker, resulting in a decrease of the surface area in contact with the polymer and a smaller T_g shift compared to the highly dispersed graphene (Ramanathan, 2008); (iii) the wrinkled structures and large specific surface area of graphene sheets likely induce strong interfacial interactions with polymer chains and substantially larger influence on the thermal properties of the matrix (Fang, 2009), even probably affect the curing reaction rate by changing the maximum exothermic heat flow temperature (Wu, 2004). Such effect has been suggested by the previous molecular dynamics studies in which the polymer mobility was altered due to geometric constraints at nanofiller surfaces (Smith, 2002). On the other hand, in some epoxy composites with functionalized graphene, the decreased degree of cross-linking induced by partial absorption/reaction of the curing agent even led to a drop in T_g value (Bao, 2011; Fang, 2010b).

Thermal expansion is another important property of graphene/polymer composites since graphene has a negative coefficient of thermal expansion (CTE), high specific surface area, and high stiffness. Therefore, graphene can prevent dimensional changes of polymers when incorporated and oriented appropriately (Kim, 2010a). The GNP suppresses thermal expansion of PP as effectively as other carbon fillers such as CB and CNF, especially in the direction of platelet alignment (Kalaitzidou, 2007). Wang and co-workers demonstrated the addition of GO into epoxy reduced the CTEs of the composites, and the effect increases as more graphene is added. The CTE of a graphene/epoxy composite was lowered by nearly 32% for temperatures below the T_g of the matrix at 5 wt% loading (Wang, 2009c). Kim and Macosko found that RGO is only marginally better or even less effective than graphite in improving dimensional stability of glassy polymers despite the higher aspect ratio (Kim and Macosko, 2008; Kim, 2009a), which is likely attributed to the lower reinforcement efficiency of RGO to its wrinkled structure and flexibility.

7.4.5 Other properties

In addition to the abovementioned mechanical, electrical, thermal conductivity, thermal and dimensional stability as well as glass transition temperature, many other important properties of graphene/polymer composites, such as dielectric property (Dimiev, 2013; Shang, 2013; Tian, 2014; Wang, 2013a; Wang, 2011b), gas permeability (Kim and Macosko, 2009a; Kim, 2010b; Wu, 2012b), microwave absorption (Bai, 2011b; Basavaraja, 2011; Singh, 2012; Wang, 2011a), and tribological performance (Huang, 2013b; Kandanur, 2012; Lin, 2013b; Shen, 2013c), were also investigated. Although these functional properties

have only been studied for a few years, graphene/polymer composites have shown promising and ideal materials for prospective technological applications. Based on the percolation theory, conductive fillers/polymer composites exhibit an insulator-conductor transition when the metal concentration is increased resulting in a large enhancement of the dielectric constant near the percolation threshold (Qi, 2005). For instance, Shang and co-workers prepared the graphene-polyaniline (PANI) nanoflakes (GPNs) (Shang, 2013), and the results revealed that the PANI layer played an active role in the dielectric properties of GPNs/PVDF composites. Compared to graphene/PVDF composites, the GPNs/PVDF composites showed a small dielectric loss (~ 0.04), high break downfield (275.0 MV/m), and large energy density (3.10 J/cm^3).

A 'tortuous path' of 2-D platelet percolating network is effective to inhibit molecular diffusion through the matrix, thus resulting in significantly reduced permeability relative to the neat matrix polymer (Paul and Robeson, 2008). In particular, orientation of the platelets may further enhance barrier properties perpendicular to their alignment, while higher platelet aspect ratios correlate with increased barrier resistance. Accordingly, the 2-D GO-derived sheets have been used for improving gas permeability of polymer materials. Kim and Macosko indicated that a 39% reduction in the nitrogen permeability of a polycarbonate composite at approximately 3.5 wt% loading of thermally treated GO (Kim and Macosko, 2009a). In their another work (Kim, 2010b), phenyl isocyanate-functionalized graphene oxide were reported to endow superior barrier properties (99% reduction in nitrogen permeability) of thermoplastic PU at approximately 3.7 wt% loading relative to an 81% reduction for TRGO at the same loading; and the barrier properties correlated with modulus improvements suggest better filler alignment or higher aspect ratio for the functionalized graphene oxide/PU composites.

The residual defects and groups in CRGO cannot only improve the impedance match characteristic and prompt energy transition from contiguous states to Fermi level, but also introduce defect polarization relaxation and groups' electronic dipole relaxation, which are all in favor of electromagnetic wave penetration and absorption (Wang, 2011a). The CRGO sheets show enhanced microwave absorption compared with graphite and CNTs, exhibiting a promising prospect as microwave absorbing material. Bai et al. prepared CRGO/poly (ethylene oxide) (PEO) composites by simply mixing GO with PEO and in situ reducing GO by *L*-ascorbic acid (Bai, 2011b). The PEO composites with uniformly dispersed CRGO have a high permittivity, and a 2.6 vol% CRGO/PEO composite with a thickness of 1.8 mm shows a high microwave absorbing capacity with a minimum reflection loss of -38.8 dB. This is attributed to the huge number of electrical pathways formed by the CRGO in the PEO matrix, which can effectively dissipate microwave energy into heat, as well as dielectric relaxation and interface scattering induced by large CRGO/PEO interfaces. Similar improved microwave absorbing properties of a TRGO/nitrile butadiene rubber composite (Singh, 2012), and the calculated reflection loss value of a composite of 10% TRGO by weight in NBR matrix is quite high, i.e. 57 dB at 9.6 GHz and reflection loss (>10

dB) over a wide frequency range 7.5-12 GHz at a thickness of 3 mm. Due to their light weight and high value of microwave absorption, this kind of RGO/polymer composite materials have wide potential in civil and military fields.

Koratkar and co-workers reported that TRGO sheets served as excellent wear reducers when incorporated as fillers in a polytetrafluoroethylene (PTFE) matrix (Kandanur, 2012), and the high $\sim 0.4 \times 10^{-3}$ mm³/Nm steady-state wear rates of PTFE were found to decrease ~ 10 -fold and ~ 50 -fold upon the inclusion of merely 0.32 and 0.80 wt% TRGO sheets, respectively. Notably, more dramatic ~ 1700 -fold and ~ 4000 -fold decreases in wear rate were observed when the filler content was increased to 5 and 10 wt%, respectively. Such TRGO sheets were also found to be significantly more effective in wear reduction than conventional micro-scale graphite. Huang et al. prepared modified RGO/PI composites via a two-stage process consisting of surface covalent modification of RGO grafting with small molecule segments and in situ polymerization (Huang, 2013b); and the results revealed that, compared to pure PI, the PI-based composites with 2 wt% modified RGO exhibited a 20-fold increase in wear resistance and a 12% reduction in friction coefficient.

7.5 Applications of graphene/polymer composite materials

According to the above review on synthesis of graphene, fabrication and properties of graphene/polymer composites, graphene shows a promising filler to improve the mechanical, electrical, thermal, and other important properties of polymers. Though numerous challenges remain in developing a fundamental understanding of graphene derived materials and their polymer composites, these materials have already been explored for wide potential applications in many fields including structural reinforcement and functional materials. The use for reinforcement, electronic memory device, sensor, photoelectric conversion and energy storage, photoelectric and biomedical application has been mostly studied.

7.5.1 Structural reinforcement materials

The significant improvement on the mechanical performance of polymer matrices can be obtained at a low graphene loading, suggesting the use of these materials in transport applications requiring the combination of high strength and light weight. In particular, the use of graphene and its derivatives opened up the possibility to further enhance the mechanical properties of the traditional fiber reinforced polymer composite systems. Yavari et al. found only $\sim 0.2\%$ (with respect to the epoxy resin weight and $\sim 0.02\%$ with respect to the entire laminate weight) of RGO additives enhanced the fatigue life of the glass fiber/epoxy composite in the flexural bending and uniaxial tensile mode by up to 1200- and 3-5- folds, respectively. The fatigue life increase (in

the flexural bending mode) with RGO additives was 1-2 orders of magnitude superior to those obtained using CNTs; and directly spray-coating the RGO at the fiber-matrix interface yielded significant benefit over uniform dispersion of RGO in the bulk epoxy resin (Figure 7.12a). In situ ultrasound analysis of the composite during the cyclic fatigue test suggested that the RGO network toughens the fiberglass/epoxy-matrix interface and prevents the delamination/buckling of the glass microfibers under compressive stress (Yavari, 2010). Similarly, graphene oxide was also used to modify the surface of carbon fibers (Huang, 2013a), which provided improved interfacial properties in carbon fiber/polymer composites (Zhang, 2012b). As a result, significant enhancement of interfacial shear strength (IFSS), interlaminar shear strength (ILSS), and tensile properties was achieved in the composites when low loading (~5.0 wt%) of GO introduced on the fiber surface. In addition, the combined use of carbon fiber and graphene nanoplatelet produced dramatic mechanical and thermal increments of thermoplastic composites (Yang, 2013b). These high performance hierarchical materials show potential to improve the safety, reliability, and cost effectiveness of fiber-reinforced polymer composites that are increasingly the material of choice in the aerospace, automotive, marine, sports, biomedical, and wind energy industries.

Graphene and its derivatives can be used to reinforce polymer fibres through solution and melt compounding methods such as melt spinning method or electrospinning, showing potential applications of fiber composites in optical fibres, smart fabrics and woven materials (Bao, 2010; Matsumoto, 2013; Shin, 2012). A membrane made of electrospun graphene/PVA fibers demonstrated its capability as a saturable absorber with wideband absorption and as efficient photonic material for the generation of ultra-short pulses in fiber lasers; and a small loading (0.07 wt%) of functionalized graphene enhances the total optical absorption of PVA by 10 times (Bao, 2010). A superior and tough PVA based composite fibre was synthesized through the hybridization of wrinkled RGO flakes and SWNTs (Shin, 2012). The hybrid fibers can be shaped into high-modulus helical springs and showed gravimetric toughness of ~1,000 Jg⁻¹, and this toughness value is far exceeding spider dragline silk (165 Jg⁻¹) and Kevlar (78 Jg⁻¹). Recently, a graphene nanoribbon (GNR)/carbon composite nanofibers were prepared by electrospinning from poly(acrylonitrile) containing graphene oxide nanoribbons (GONRs), and successive twisting and carbonization (Matsumoto, 2013). During electrospinning, the well-dispersed GONRs were highly oriented along the fiber axis in an electrified thin liquid jet, and the carbonization of the matrix polymer enhanced the mechanical electrical properties of the composites. Such GNR/carbon composite nanofibers could be applied to reinforcements for lightweight composites and high-performance electrodes for fuel cells, fiber-shaped solar cells, secondary batteries, and capacitors, including flexible and wearable electronic devices.

Due to the unique structure and high thermal stability, graphene can also serve as an alternative to the conventional flame retardants since it may act as a barrier hindering transfer of combustion gases into the flame zone and energy feedback and then retarding combustion. Hu and co-workers investigated the flame behavior

of epoxy composites containing EG, GO, organic phosphate functionalized GO (FGO) and CRGO (Guo, 2011c). The flame retardant properties measured by micro combustion calorimeter revealed that both CRGO/epoxy and FGO/epoxy composites performed better than GO/epoxy composites in flame retardant properties with a maximum reduction of 23.7% in peak-heat release rate when containing 5 wt% FGO and a maximum reduction of 43.9% at 5 wt % loading of CRGO. Similar flame retardant graphene/polymer composites were also developed and investigated during the past several years (Bao, 2012; Guo, 2011c; Higginbotham, 2009; Liu, 2014a) and showed potential application for flame retardation. In addition, RGO sheets in polymer foams were also demonstrated the simultaneous enhancement of the compression strength, with an increase in the normalised modulus of more than 200%, and thermal stability, with an increase of the decomposition temperature of nearly 60 °C, with loading fractions as low as ~0.25 wt% (Verdejo, 2008). These lightweight and multi-functional graphene/polymer foams are versatile materials, showing potential to be widely used in transport, construction, electron, packaging applications (Eswaraiah, 2011b; Hodlur, 2014; Shen, 2012a; Verdejo, 2008; Wu, 2013b; Wu, 2013c; Zhang, 2011).

Aside from mechanical reinforcement, a host of diverse applications have been envisioned for graphene-based polymer composites, all harnessing the other mechanical property improvements were discussed in the previous sections. Incorporation of graphene and its derivative can significantly reduce gas permeation through a polymer composite relative to the neat matrix polymer (Potts, 2011a). The combination of the improved barrier properties and increased light absorption of a graphene/PS composite versus neat PS suggests wider application as a packaging material (Compton, 2010b). The mechanical reinforcement of graphene/polymer composites together with suppression effect of graphene in the generation of wear debris, and protective effect of graphene against the friction force, offers potential application as superior wear resistant materials (Kandanur, 2012).

7.5.2 Functional materials

The intrinsic high electrical and thermal conductivities as well as large aspect ratio of graphene enable the attainment of percolation thresholds in polymer materials at a very low loading, making them as functional materials from sensors to flexible conductor, photovoltaics, energy storage, electrostatic discharge and electromagnetic interference shielding materials.

7.5.2.1 Sensors

The sensing responses of graphene/polymer composite materials could be categorized into two main facets, including strain and damage sensing (Cai, 2014; Chiacchiarelli, 2013; Du, 2008; Goncalves, 2014; Hou, 2013b; Kuang, 2013; Kujawski, 2010; Li, 2012b;

Ramanathan, 2007) and temperature sensing (Hewitt, 2013; Mahmoud, 2012; Quan, 2009; Syurik, 2013; Zhang, 2014). The overall conductivity of graphene/polymer composites depends strongly on the tunnelling between local conductive networks; hence, a change in the local tunneling distance would produce a significant change in the conductivity. Therefore, outer-stimuli-induced changes in the tunneling distance could result in a significant change in the conductivity, which can be monitored and used for sensing purposes (Sadasivuni, 2014).

Graphene and its derivatives, including GNP, GO and RGO sheets, can be incorporated into an insulating polymer matrix to fabricate strain sensors (Al-Solamy, 2012; Eswaraiah, 2011a; Goncalves, 2014; Kim, 2011b; Kuang, 2013). When an external pressure is applied, the conducting network of electrically conductive composites changes, and this results in resistance variation. This is so-called piezoresistive effect, which can provide simple and direct energy/impulse dependence relative to the mechanical and electrical domains. A wide range of applications have been proposed for piezoresistive materials, including smart textiles, health monitoring, wearable electronics and movement sensors (Yamada, 2011). Chen and co-workers prepared the piezoresistive GNP/silicone rubber composites (Chen, 2007), and the composite with 0.0136 vol% GNP loading which is close to the percolation threshold presents a sharp positive-pressure coefficient effect of the resistivity under very low pressure, namely, in the finger-pressure range (0.3-0.7 MPa). This rapid transition behavior is due to the compressive-stress-induced deformation of the conducting network. The good dispersion state of GNPs throughout the silicone rubber matrix produced insufficient conductive paths between the fillers under applied pressure. Cheng and co-workers synthesized 3-D foam-like graphene macrostructures by template-directed chemical vapour deposition and then prepared the graphene/PDMS composites (Chen, 2011). The results revealed that with a graphene loading as low as ~0.5 wt%, graphene/PDMS composites showed a very high electrical conductivity of ~10 Scm⁻¹. In particular, the resistance of the composite was increased through the first three cycles of bending and straightening, it became stable and the electrical resistance increase remained constant at only ~7% from the fourth cycle under bending, compared with that when straightening (Figure 7.12b). Such unique network structure and the outstanding electrical and mechanical properties of graphene foams showed great potential for flexible, foldable and stretchable conductors. Similarly, Zhang and co-workers coated graphene sheets or ribbons onto pre-stretched PDMS films and formed periodically buckling structures after the strain release of the PDMS film (Wang, 2011g). The rippled and buckled graphene/PDMS composites as flexible strain sensors showed resistance changes under different strains, and the resistances were linearly decreased from 5.9 to 3.6 kΩ with the increase of strains from 0 to 20% in the case of the rippled graphene, while they were linearly increased when the strain was improved from 0 to 25% for the buckled graphene.

Temperature has a substantial impact on the conductivity of polymer composite materials due to the thermal expansion or melting of the matrix with increasing

temperature (Dai, 2012; Hewitt, 2013; Mahmoud and Al-Ghamdi, 2012; Rybak, 2010; Syurik, 2013; Zhang, 2014). Thus, this characteristic can be used as temperature sensors, self-regulated heaters and over-current protectors. Mahmoud et al. investigated the influence of temperature on the electrical conductivity of GNPs/rubber composites with different filler loadings ranging from 1% to 5%, and observed the dependence of both temperature and filler loading on conductivity (Mahmoud and Al-Ghamdi, 2012). This increase in conductivity is due to the decrease in the hopping path between GNP layers as the amount of GNP in the rubber matrix increases. Syurik et al. studied the temperature dependence of electrical conductivity of GNPs/PS composites (Syurik, 2013). The results revealed that for low loadings of GNPs the conductivity behaviour changed significantly within the temperature range of 295-369 K. The conductivity saw a drop with decrease of temperature from 369 to 331 K, while a slight decrease of conductivity was observed within the temperature range of 331-305 K. Within the low-temperature range of 305-295 K a growth of conductivity was explained by increasing of electron tunnelling through the contact caused by the creation of electret state. The observed dependence of conductivity upon temperature is non-linear for low loadings of GNPs and it is close to the linear dependence for higher loadings of the filler.

Due to the combination of extraordinary optical, electrical, thermal and mechanical properties, graphene and its derivatives can also function as “energy transfer” in various actuators (Ansari, 2013). Cheng and co-workers demonstrated that the graphene/PU composites showed an excellent light-triggered actuation with enhanced mechanical properties (Liang, 2009b). It was found that the composites containing ~1.0 wt% sulfonated functionalized graphene exhibited intriguing and repeatable actuations performance which can strikingly contract and lift a 21.6 g weight 3.1 cm with 0.21 N of force on exposure to infrared light and demonstrate estimated energy densities of over 0.33 J/g, and the highest energy density reached ~0.40 J/g. In addition, the graphene/polymer composites had been also studied for electromechanical actuators and thus have attracted increasing interests for various applications such as artificial muscles, microrobotics, switches and microscopic pumps (Huang, 2012b; Liang, 2012). Compared to traditional electromechanical actuators made of electroactive polymers, conducting polymers and ferroelectric ceramics, graphene represents a new and promising candidate for electromechanical actuators due to the high conductivity and a negative thermal expansion coefficient. By incorporation of the graphene and its derivatives into various polymers, a variety of electromechanical composite actuators with excellent sensing properties had been prepared (Kim, 2014; Lian, 2010; Liu, 2012a; Lu, 2013; Ramasamy, 2014). For example, Liang et al. prepared a graphene/polydiacetylene bimorph actuator and obtained a large actuation motion with curvature of appropriately 0.37 cm^{-1} at a current density of 0.74 A/mm^2 and high actuation stress of more than 160 MPa/g for an applied direct current of 0.29 A/mm^2 (Liang, 2012); and such composite actuator exhibited reversible swings under alternating currents and showed a long cycle life under high frequencies up to 200 Hz.

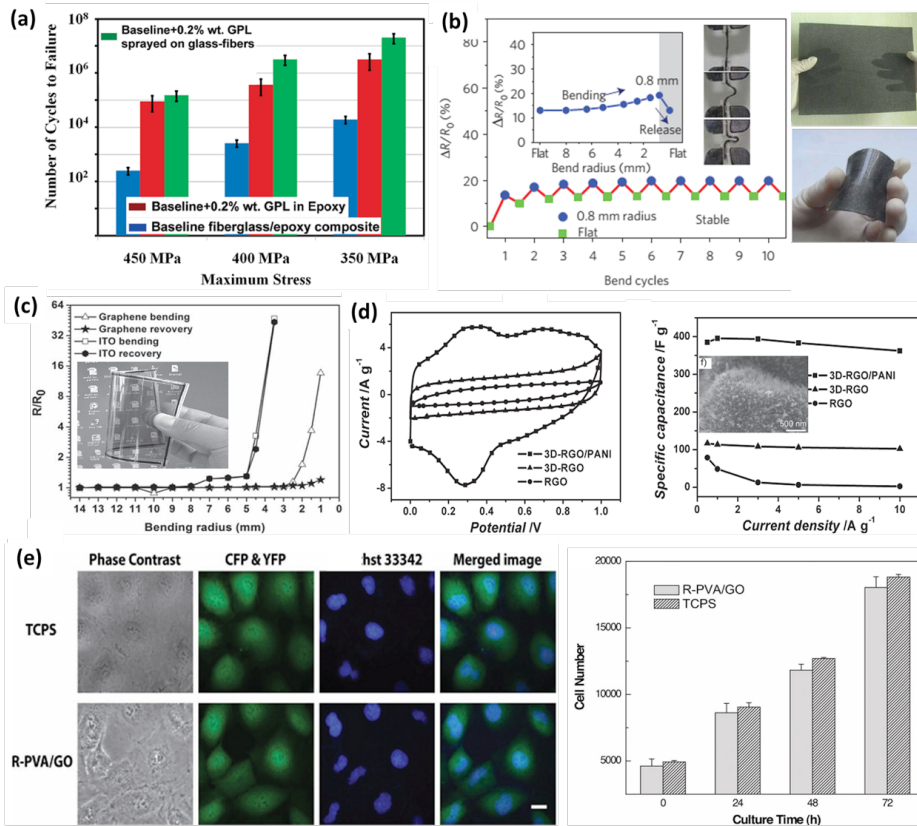


Figure 7.12. Graphene/polymer composite application as structural reinforcement and functional materials: (a) flexural bending fatigue results comparing performance of three-phase composites with RGO dispersed into the bulk epoxy resin vs. the same amount of RGO by weight directly sprayed onto the glass microfibers (Yavari, 2010); (b) electrical resistance change of a graphene/PDMS composite under bending and then straightening for each cycle (left inset: the resistance variation of the composite in a typical bend cycle after becoming stable, right inset: bending process), and photographs of a free-standing graphene foam (GF) and a bent GF/PDMS composite, showing its good flexibility (Chen, 2011); (c) electrical resistance change with tensile strain applied to RGO and ITO films on PET substrates under bending and unbending conditions (inset: a flexible RGO/PET film) (Wang, 2012a); (d) electrochemical performance of the RGO film, 3D-RGO film, and 3D-RGO/PANI film: right) CV curves in the potential range and left) specific capacitance at different current densities (inset: SEM images of cross-section of the hierarchical composite film) (Meng, 2013); and (e) biocompatible properties of a RGO/PVA composite: right) phase contrast and fluorescence images of HUVECs grown on TCPS plates and RGO/PVA coated surface for 48 h (The phase contrast images, the green fluorescence from the CFP-DEVD-YFP4 fusion protein, and the blue fluorescence from Hoechst 33342 were recorded from the same observation field in the phase contrast, green, and blue channels, respectively. The scale bar represents 50 μm for all the images. Cell viability of HUVECs on TCPS and a RGO/PVA-coated surface after being cultured for different time (Li, 2012d).

7.5.2.2 Flexible conductor

Flexible conductor can maintain the high electrical conductivity when highly stretched or bended, which has created exciting opportunities and has attracted intensive interest in recent year (Chae, 2013; Choi, 2012a; Chun, 2010). As indicated by the name, a combination of good mechanical flexibility and high electrical conductivity is required for flexible conductors, which is potential for applications in robot arm joints, wearable displays, flexible electronics, dielectric elastomer actuators, stretchable solar cells, supercapacitors, lithium-ion batteries, and field emission devices (Deng, 2014).

Considering the excellent mechanical and electrical properties of graphene and its derivatives, they have been used to prepare flexible conductor (Chen, 2013b; Cong, 2013c; Hou, 2013a; Kim, 2009b; Lee, 2014; Liang, 2014; Liu, 2012b; Seol, 2012; Tuukkanen, 2014; Wang, 2012a; Yu, 2013a; Yu, 2013b). In general, two main strategies are employed: (i) the traditional compounding of conductive graphene fillers into a polymer matrix and (ii) the use of some novel preparation methods. The first strategy for obtaining a flexible conductor is to compound a conducting graphene into a rubbery polymer matrix (e.g. poly(acryloyl-6-aminocaproic acid) and PDMS) to form elastic composites (Chen, 2013b; Cong, 2013c; Hou, 2013a; Liu, 2012b; Seol, 2012). Graphene/polymer composites with a low filler loading can produce highly elastic conductors with a strain higher than 100% (Liu, 2012b), yet the conductivity is typically too low for use as a flexible electronic device. The composites with a high filler loading can produce devices with a high level of conductivity but with poor flexibility due to the segregation or agglomeration of the fillers (Seol, 2012). An effective method for fabricating a highly conductive and stretchable composite can be obtained by backfilling a preformed graphene/MWCNT aerogel with PDMS, and the electrical conductivity reached 2.8 S/cm with only 1.3 wt% graphene/MWCNT loading, and remained constant after 100 times repeated stretching by 20% and 5000 times bending (Chen, 2013b).

In the second strategy, a flexible conductor can be developed by integrating conductive graphene-based fillers onto a flexible substrate using various technologies such as rod-coating (Wang, 2012a), etching and transfer processes (Kim, 2009b), room temperature rubbing (Yu, 2013a; Yu, 2013b). For instance, Kim et al. developed a simple method to grow and transfer high-quality stretchable graphene films on a large scale using CVD on nickel layers, which can easily be transferred to stretchable substrates (such as PDMS) by simple contact methods (Kim, 2009b). Similarly, the rod-coating technique was successfully used to fabricate a flexible RGO-based film with a low resistance and good transparency prepared directly on PET substrates (Wang, 2012a). A fully functional 4.5 inch four-wire resistance touch screen fabricated using the RGO/PET film showed not only a linearity comparable to ITO-based touch screens, but also a high mechanical flexibility exceeding that of ITO-based touch screens (Figure 7.12c), indicating an approach potentially suitable for the roll-to-roll production of usable RGO films for various flexible electronic devices. Recently, the

graphene-based hybrid fillers were also used for transparent conductive electrodes with high surface conductivity, high transmittance in the visible wavelength range, and mechanical compliance. Liang et al. prepared a transparent conductive electrode (ICE) based on a silver nanowire (AgNW) percolation network modified with graphene oxide (Liang, 2014), and the graphene oxide-soldered AgNW (G-s-AgNW) network has a figure-of-merit sheet resistance of 14 ohm/sq with 88% transmittance at 550 nm. Composite ICE fabricated by inlaying a G-s-AgNW network in the surface layer of polyurethane acrylate films is stretchable, by greater than 100% linear strain without losing electrical conductivity.

Graphene/polymer composites have been widely studied for polymer solar cells and other optoelectronic applications as a new family of photovoltaic devices (Beliatis, 2014; Chao, 2013; Choe, 2010; Hsu, 2012; Kim, 2011a; Li, 2010; Li, 2011d; Park, 2013a; Stratakis, 2014; Yang, 2012b; Yusoff, 2014). Photovoltaics and optoelectronics mainly rely on the fact that monolayers of graphene are about 98% transparent but still have high electrical conductivity. This feature makes graphene-based materials potentially well-suited to address issues related to photoexcitation and exciton mobility/diffusion as transparent conducting electrodes (Potts, 2011a). A lot of edges of graphene provided it with higher electrocatalytic activities in the use for counter electrodes in polymer solar cells than CNTs as the edge of such carbon nanomaterials was much more effective for the catalysis of redox interaction than the side part (Sun, 2013c). Yu et al. prepared a bilayer polymer solar cell based on the graphene/poly(3-hexylthiophene)/C60 heterostructure with an efficiency of 0.61%, which is three times of the poly(3-hexylthiophene)/C60 heterostructure (Yu, 2010). A theoretical study predicted that a much higher efficiency of over 12% may be achieved for polymer solar cells based on the graphene/polymer composite (Yong, 2010). Although current results revealed that overall efficiencies for these devices are still relatively low when applied as organic photovoltaics, there is still much room for improvement in these devices by optimizing the structure of composite materials.

Advanced energy storage technologies and systems have attracted considerable interest due to continuously increasing demand for more energy and projected exhaustion of fossil fuels. Due to the low dielectric loss, high electric breakdown field, low cost, and robustness, polymer based composites are the materials of choice for energy storage applications (Huang, 2014). To enhance the electrical energy density of polymer, an effective approach is to disperse high dielectric constant ceramic powders or conductive fillers into the polymer matrix. Unfortunately, the concentration of the ceramics must typically be over 50 vol% in order to achieve a high dielectric constant but such a large content may adversely affect the mechanical properties of the composites (Wang, 2004). Recently, graphene-based composites incorporating PANI and other conducting polymers have been studied for energy storage (Lu, 2012b; Wang, 2009a; Wu, 2010a; Xu, 2011; Zhou, 2013). In general, graphene may exhibit high mechanical and thermal stability and high electrical conductivity while shows a relatively low electrochemical activity; while polymers are found to demonstrate

high electrochemical activity but with low stability and conductivity. Thus, the formation of graphene/polymer composites may combine their advantages for high performances in energy storage. In particular, specific capacitances reported from 210 F/g to over 1000 F/g have been reported for the PANI-based composites containing different graphene structures (Cong, 2013b; Kumar, 2012; Li, 2011a; Li, 2013f; Liu, 2014b; Lu, 2011; Sarker, 2012; Wang, 2013c; Xu, 2014; Xu, 2010a; Yan, 2010b; Zhang, 2010d). For example, Wei and co-workers fabricated hierarchical porous graphene/PANI composite film formed by the polymerization of PANI nanowire arrays, and the flexible free-standing film exhibited excellent supercapacitor rate performance with a retention of 89% as current density was varied from 0.5 to 10 A/g arrays, the specific capacitance reached up to 385 F/g at 0.5 A/g, with a rate retention of 94% as current density was varied from 0.5 to 10 A/g (Figure 7.12d) (Meng, 2013). Similar free-standing and flexible RGO/PANI nanorods composite paper exhibited excellent supercapacitor performance with an enhanced specific capacitance (763 F/g) and good cycling stability by electropolymerization of PANI nanorods on the above graphene paper (Cong, 2013a).

With the advent of flexible electronics, flexible lithium-ion batteries have attracted great attention as a promising power source in the emerging field of flexible and wearable electronic devices such as roll-up displays, touch screens, conformable active radio-frequency identification tags, wearable sensors and implantable medical devices (Zhou, 2014a). Due to the high electrical conductivities and porous networks of graphene and electroactive properties of both graphene and conductive polymers, graphene/polymer composite materials had been also investigated for lithium ion batteries to enhance the charge/discharge rate capability and cyclic stability (Abouimrane, 2010; Bai, 2011a; Guo, 2011a; Guo, 2012a; Kundu, 2013; Liu, 2013; Song, 2012b; Sun, 2013c; Wu, 2012a; Yang, 2012c). The highly-dispersed graphene in the polymer composite drastically enhances the electronic conductivity and allows the electrochemical activity of the polymer cathode to be efficiently utilized, which allowed for ultrafast charging and discharging (100 mAh/g delivered within just a few seconds (Song, 2012b)). Other applications of the conductive graphene/polymer composites are electrostatic discharge and electromagnetic interference shielding materials (Liang, 2009c; Zhang, 2011), which offers potential uses from carpeting floor mats, and electronics packaging to mobile phone parts, telecommunication antenna, and frequency shielding coatings for aircraft and electronics.

7.5.3 Biomedical applications

Another emerging application for graphene-based composites has focused on biomedical applications in recent years owing to their biocompatibility, the ease with which they can be functionalized and their excellent properties. Potential applications for functionalized graphene sheets range from drug delivery and

multimodal imaging to exploitation of the electrical properties of graphene toward the preparation of biosensing devices (Carpio, 2012; Guo, 2012b; Hess, 2014; Lu, 2008; Luo, 2013; Unnikrishnan, 2013; Wan, 2011; Wang, 2010). For instance, Chen and co-workers prepared the RGO-filled glucose oxidase (GOx) biocomposite film, showing very good stability, reproducibility and high selectivity. In particular, the developed biosensor exhibited excellent catalytic activity towards glucose, which may open up new horizons in the production of cost-effective biosensors and biofuel cells (Unnikrishnan, 2013).

Other biocompatible and biodegradable polymer composites have also been investigated, and incorporation of graphene oxide or RGO sheets into chitosan (Fan, 2010; Zeng, 2011), PVA (Li, 2012d), Bis-GMA/tetraethyleneglycol diacrylate (Nuvoli, 2013), polyethylene glycol (Yang, 2013a), and poly(lactide) (Mittal, 2014). Composite films of chitosan and graphene have been prepared via a solution mixing, and the cell adhesion result showed that the L929 cell adhered to and developed on the composite films as well as on pure chitosan film, indicating that the graphene/chitosan composites have good biocompatibility (Fan, 2010). A hybrid building block of PVA-coated graphene oxide sheets was prepared and the RGO/PVA composite films with a nacre-like bricks-and-mortar microstructure were made through a facile solution casting method followed by a post-reduction treatment (Li, 2012d). As shown in Figure 7.12e, biocompatibility of the composite film was studied using human umbilical vein endothelial cells (HUVECs). The PVA/RGO films are suitable to support cell growth; and the number of cells of HUVECs on RGO/PVA films was almost the same as that on common tissue culture polystyrene (TCPS) plates on the days when this assay was carried out. No cytotoxicity was indicated and the seeding efficiency of HUVECs was even higher on PVA/RGO films than on common TCPS plates. Combined with outstanding mechanical properties and electrical conductivity, their biocompatible properties make these films promising candidates in biotechnology applications, such as electroactive substrates/scaffolds for tissue engineering, drug delivery, cell culture, and biosensors.

7.6 Summary and outlook

Graphene and its derivatives have been widely incorporated into polymers to fabricate multi-functional composite materials. Two main synthetic approaches i.e. bottom-up and top-down have been developed to obtain graphene and its derivatives. Unlike the bottom-up approaches, the top-down approaches involve the synthesis of graphene or its derivatives from separation/exfoliation of graphite or graphite derivatives, showing more appropriate for large-scale production required for polymer composite applications. Surface modification of graphene and its derivatives have been employed to disperse graphene into various polymers, and the corresponding conventional fabricating methods including solution mixing, in situ polymerization and melt

blending, can produce composite materials at high efficiency and with low cost, but the excellent properties of individual graphene sheets are challenges for being fully used at macroscopic scale. The template method can synthesize graphene/polymer composite materials containing 3-D porous graphene scaffolds and effectively avoid the restack of graphene in polymer.

Various properties of the graphene/polymer composites, such as mechanical properties (tensile strength and elastic modulus, fracture toughness), electrical and thermal conductivity, thermal stability and dimensional stability, dielectric property, gas permeability, microwave absorption, and tribological performance can be significantly improved at a small amount of graphene or its derivatives. Several factors including the dispersion/exfoliation and alignment of graphene and the interfacial graphene/matrix interaction play crucial roles in significantly improving mechanical properties. The fabricating techniques are important for influencing reinforcement as well as electrical and thermal properties. The combination of graphene and other fillers such as CNTs produces synergetic effects on enhancing the mechanical, electrical and thermal conductivities, showing promising to fabricating multifunctional and high performance composite materials. Based on these physical properties, graphene/polymer composites are promising as structural, functional and biocompatible composites that can be widely used in various applications, including hierarchical materials, flame retardants, sensors, flexible conductors, solar cells, microwave absorption, supercapacitors, biomedical devices, etc.

Although the advanced graphene-based polymer composites have been widely investigated, there are still many challenges that must be addressed for these composites to reach their full potential. First, the defects, introduced into RGO sheets by the oxidation to convert graphite to GO followed by thermal or chemically reduction process, might ultimately limit the electrical conductivity and mechanical properties achievable with RGO sheets relative to pristine and defect-free graphene platelets (Potts, 2011a). Thus, large-scale synthetic methods of graphene production that preserves its extended, conjugated structure may be favorable for certain demanding applications of graphene-based polymer composites. Second, although some surface modification techniques are effective to enhance the graphene/matrix interfacial interaction and thus improve the mechanical properties, they usually impair the electrical conductivity. On the other hand, the fabricating processing techniques such as sonication can reduce the aspect ratio of the exfoliated sheets, which in turn negatively affect reinforcement as well as electrical and thermal properties (Li, 2013d). The exfoliation and/or dispersion techniques that promote an ideal dispersion and interface in the composites conceivably further develop multifunctional graphene/polymer composites. Third, how to prepare structure-controlled graphene with identical geometry as well as consistent and dependable high performance is helpful to achieve further property improvements. Increased control over alignment and spatial organization of graphene and its derivatives could be beneficial to nearly all types of composite properties. Especially, much more work are needed to prepare

conductive polymer composites with low electrical percolation thresholds as reported in CNT/polymer composites. Therefore, much more effort should be paid to develop the graphene-based composite materials with remarkable and superior properties, and some high performance applications may be further achieved in the near future.

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