

Nur Bazilah Thalib, Siti Noor Hidayah Mustapha*, Chong Kwok Feng and Rohani Mustapha

Tailoring graphene reinforced thermoset and biothermoset composites

<https://doi.org/10.1515/revce-2017-0091>

Received September 20, 2017; accepted September 7, 2018

Abstract: The surge of knowledge among researchers pertaining to the excellent properties of graphene has led to the utilisation of graphene as a reinforced filler in polymer composites. Different methods of graphene preparation, either bottom-up or top-down methods, are important requirements of starting materials in producing reinforced properties in the composites. The starting graphene material produced is either further functionalised or directly used as a filler in thermoset polymer matrixes. An effective interaction between graphene and polymer matrixes is important and can be achieved by incorporating graphene into a thermoset polymer matrix through melt mixing, solution mixing or *in situ* polymerisation processes. In addition, by taking into consideration the importance of green and sustainable composites, the details of previous work on graphene reinforced bio-thermoset polymer matrixes is discussed. The resultant mechanical and thermal properties of the composites were associated to the chemical interaction between the graphene filler and a thermoset matrix. Exploration for further variations of graphene polymer composites are discussed by taking the reinforcement properties in graphene composite as a starting point.

Keywords: biocomposite; functionalised graphene; graphene filler; graphite; thermoset resin.

1 Introduction

Over the past decade, graphene has been an interesting topic of study among academicians and industry researchers (Jang and Zhamu 2008, Lin et al. 2014, Mauro

et al. 2014, Rus et al. 2015, Khan et al. 2016). The interest of graphene incorporation into polymeric materials arises from its exceptional mechanical and thermal properties such as its high Young's modulus and good thermal conductivity. Graphene is also reported to be the world's thinnest, strongest and firmest material (Paulchamy et al. 2015, Phiri et al. 2017). The properties of a composite inherit the properties of its building block. Many successful studies have proved that incorporation of graphene as a nanofiller in polymeric materials and composites has enhanced its mechanical (Rafiee et al. 2009, Naebe et al. 2014, Xing et al. 2017), thermal (Park et al. 2014, Tang et al. 2015) and electrical (Lin et al. 2014) properties. Graphene is found to have potential in many applications including structural applications (Hu et al. 2014), in semiconductors and batteries (Zheng and Wong 2003, Chang et al. 2014), in supercapacitor electrodes (Ali et al. 2015) and in the thermal management in battery packs (Pop et al. 2012, Renteria et al. 2014). Based on the contribution of graphene in reinforcing nanocomposite applications, it is important to determine the current derivative of graphene due to the advantages of graphene in various applications, relying on the structure of graphene and ways in which it can be used for the required applications.

Graphene has exceptional characteristics in reinforcing polymer nanocomposite properties based on the listed examples. Graphene reinforced polymer composite has contributed to the recognition and deep study on graphene chemistry and graphene chemical interaction with polymer matrixes. This review generally focusses on investigating the properties of graphene by considering its remarkable characteristics. Previous studies that discussed graphene/polymer nanocomposite have focussed on the fabrication of graphene and the fabrication of graphene nanocomposites (Phiri et al. 2017). The analysis mainly focusses on various examples of graphene/polymer nanocomposites, rather than the fundamental reasons to reinforce mechanical and thermal properties of the polymer composites. Thus, this paper presents an overview of the chemical interaction between graphene and a polymer matrix to improve the mechanical and thermal properties of the resulting composite, as well as the general practice in preparing graphene filler and processing graphene/polymer nanocomposites. In addition, the spur of environmental concern, depleting petroleum

*Corresponding author: Siti Noor Hidayah Mustapha, Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia, e-mail: snhidayah@ump.edu.my. <https://orcid.org/0000-0002-4107-6074>

Nur Bazilah Thalib and Chong Kwok Feng: Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Rohani Mustapha: School of Ocean Engineering, Universiti Malaysia Terengganu, 21030, Kuala Terengganu, Terengganu, Malaysia

resources, and the success of past studies on bio-based polymer nanocomposites, graphene/bio-based thermoset nanocomposites are highlighted (Haq et al. 2011, Albayrak 2013, Mustapha et al. 2014).

2 Graphene

Graphene has a unique structure. It is arranged in many hexagonal lattices by sp^2 hybridised bonded carbon atoms (Potts et al. 2011, Young et al. 2012, Phiri et al. 2017). The multiple hexagonal lattice joined by carbon bonds forms a two-dimensional (2D) single layer graphene (Potts et al. 2011, Young et al. 2012, Phiri et al. 2017). This building block is the basic structure of

graphitic materials, also known as carbon allotropes (Potts et al. 2011, Young et al. 2012, Rohini et al. 2015, Phiri et al. 2017). The allotropes such as zero-dimension fullerenes, one-dimensional (1D) carbon nanotube and three-dimensional (3D) nanostructure from staggered sheets are all formed from structural modification of the graphene sheet as shown in Figure 1.

Graphene and graphite are of the same sp^2 hybridised bonded carbon in planar form but are different in the arrangement of the lattice. In this review, graphene is referred to as a one-layer planar carbon-carbon (C-C) bond, while graphite is multiple layers of graphene in a staggered form forming a 3D order as shown in Figure 2. Graphene is an sp^2 hybridised bonded carbon atom with one free electron to be used in reactions and to

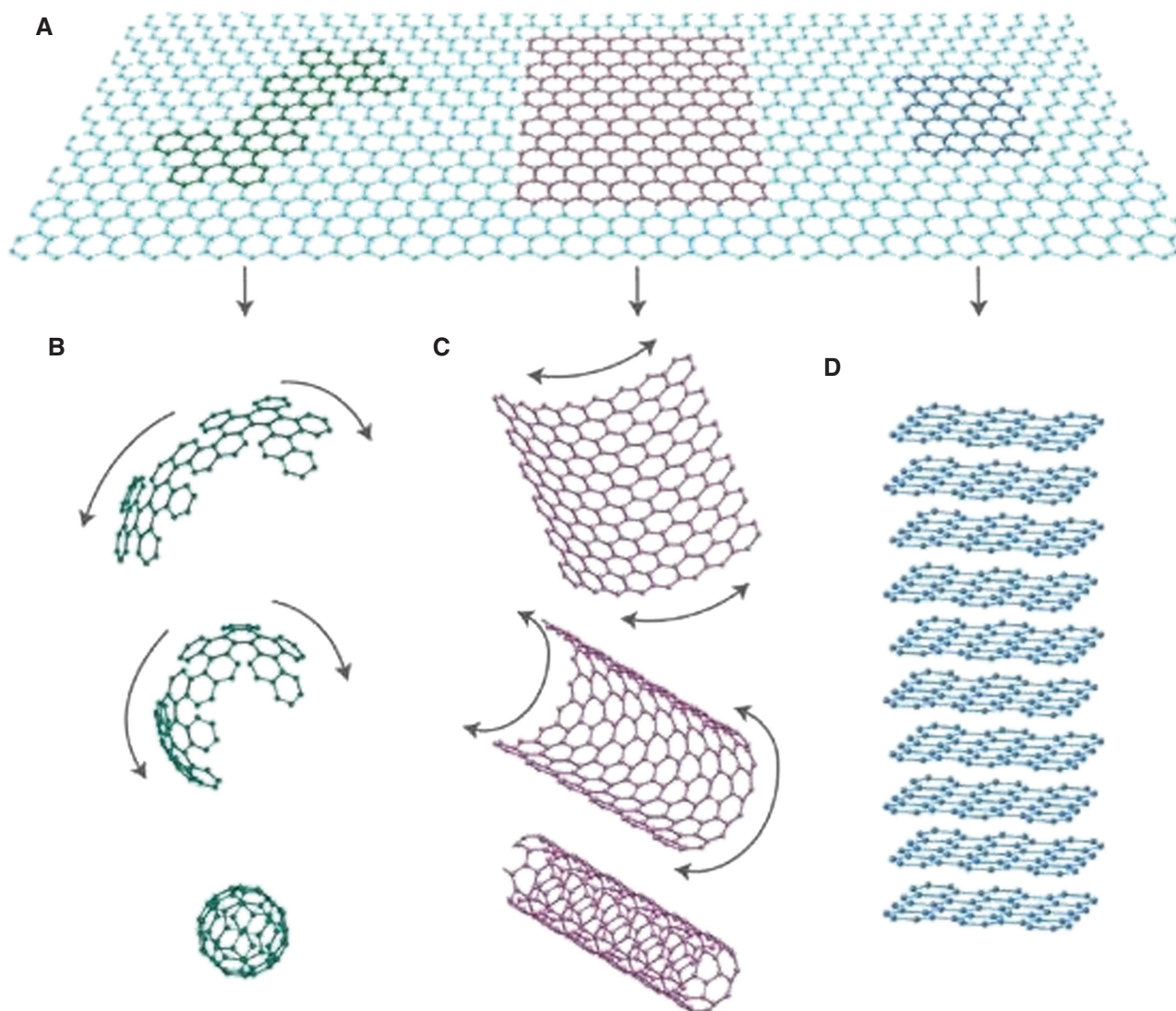


Figure 1: The structure of graphene with four different allotropes.

(A) 2-D graphene (B) 0-D fullerene (C) 1-D carbon nanotube and (D) 3-D graphite. Reprinted with permission from Macmillan Publishers Ltd: [Nature Materials] (Geim and Novoselov 2007), copyright (2007).

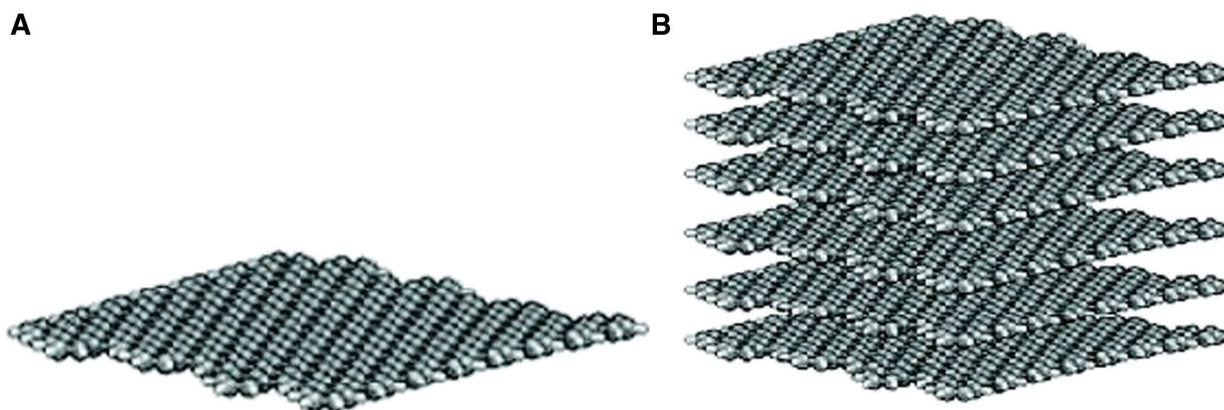


Figure 2: Graphene from single layer to multiple layers to form graphite. Representation of (A) graphene sheet and (B) graphite. Reproduced (in part) from (Ciesielski and Samori 2014) with permission from The Royal Society of Chemistry.

complete the sp^3 hybridised structure to form derivatives of graphene.

In 2014, Inagaki and Kang reviewed graphene derivatives including hydrogenated graphene, fluorinated graphene and graphene oxide (GO). Hydrogenated graphene or graphane consists of an sp^3 C-C bond compared to the sp^2 C-C bond of graphene. It was synthesised in 2009 firstly through a graphene reaction with cold hydrogen plasma at low pressure and temperature (Inagaki and Kang 2014). Graphene has insulating electronic behaviour and a reversible tuneable crystal structure and is a great prospect in nanoscale device application, hydrogen storage, carbon dioxide (CO_2) filters, sensing platforms for trinitrotoluene (TNT) in sea water, biomarkers (Peng et al. 2014, Sahin et al. 2015) and graphene based electronic circuits (Lee et al. 2017). Different from graphane, fluorinated graphene or fluorographene with fluorine functionalities on graphene represent different characteristics to graphene. Incorporation of the fluorine atom to the carbon lattice gives rise to an electronic band opening and optical transparency of fluorinated graphene (Chronopoulos et al. 2017). Fluorine binds more strongly to the carbon lattice compared to hydrogen. It leads to higher thermally stable and chemically inert fluorographene. The properties of fluorographene had widened the research of the material in as regards lubrication, in batteries, supercapacitors, biosensors, solar cells technologies, electrocatalytic applications, oil-water separation, gas separation and many more applications (Chronopoulos et al. 2017).

Among all, GO attracts the greatest attention because it is cheap, easily accessible (Potts et al. 2011) and a good candidate for use in many applications (Dreyer et al. 2009). GO is oxidised graphene, with oxygen functional molecules on both sides of graphene sheet surface and edges

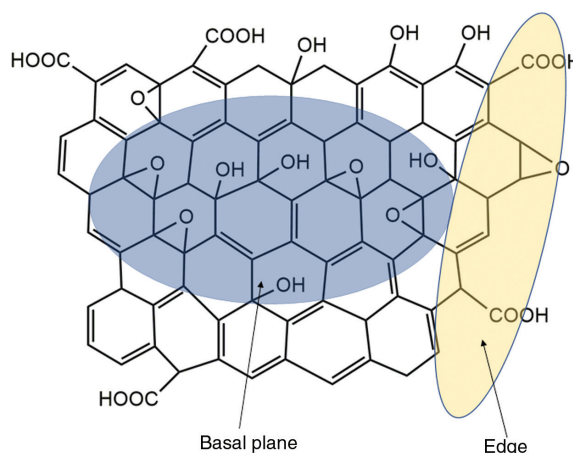


Figure 3: The structure of GO with hydroxyl and epoxy functional groups at basal plane and edge of graphene sheet. Reproduced (adapted) from (Dreyer et al. 2009) with permission from The Royal Society of Chemistry.

of the graphene sheet (Potts et al. 2011). The illustration is shown in Figure 3. The chemical functionalization of graphene with reactive oxygen functional groups widens the opportunity to create chemical or covalent interactions of graphene with the host structure of the material for enhancement in mechanical and thermal properties.

3 Graphene preparation

In recent works, there are two possible methods that have been developed to synthesise nanomaterials and to fabricate nanostructures, which is the bottom-up approach and the top-down approach. The methods can be applied to nanoscale graphene preparation. In previous studies,

graphene has been widely explored and synthesised using various common routes including reduction of GO through chemical, electrochemical and thermal reduction, chemical vapour deposition, and chemical exfoliation.

3.1 Bottom-up graphene synthesis technique

In bottom-up methods, the preparation of graphene starts with a small entity to a larger build-up of the graphene nanostructure (Tour 2013). The fabrication of nanocomposite through the bottom-up method has been applied on a laboratory scale. In the latter section, the bottom-up approach to produce graphene through chemical vapour deposition and organic chemistry reaction is discussed.

3.1.1 Chemical vapour deposition

Chemical vapour deposition (CVD) is a process where the carbon precursor is diffused onto a transition metal substrate at a growth temperature, and upon cooling the metal, carbon will be precipitated on the bulk metal (Galpaya 2015). Due to the needs of the metal substrate to grow graphene, the metal substrate is also referred to as a catalyst in later explanations. The intended structure of the graphene end product can be determined from the structure of the metal catalyst used. For example, the shape of the carbon nanotube (CNT) can be produced with CVD with the spherical shape of the catalyst nanoparticle while the graphene sheet grows on a layer of metal sheet (Awadallah et al. 2017).

Contamination is an issue that might arise during graphene growth and the issue can be avoided by using an inert metal catalyst. Nam et al. (2017) conducted an experiment on the chemical vapour deposition of graphene on platinum and studied the growth of graphene and its interaction. The presence of graphene was proven as evidenced by G-peaks, 2D and D-peaks in Raman spectroscopy. The G-peak for the C-C stretching bond was observed at 1580 cm^{-1} , the 2D-peak for the sp^2 carbon system at 2700 cm^{-1} and the D-peaks at around 1350 cm^{-1} . The inert platinum metal is unaffected by oxidation; thus it is ideal to grow a uniform graphene monolayer. However, larger growth of graphene requires a larger size of platinum film due to the low carbon solubility in platinum compared to nickel (Kang et al. 2009). Therefore, platinum is an expensive choice to grow graphene due to its price and larger size of platinum required to grow a larger graphene. Possible metals to grow graphene include cobalt- (Amato 2018), nickel- (Al-Shurman and Naseem

2014) and iron- (Zheng et al. 2017) based catalyst. In a study conducted by Awadallah et al. (2017), a graphene nanoplatelet (GNP) was prepared with the three iron substrate catalysts. Among the three metallic sheets, metallic nickel (Ni) grew more graphene layers and enhanced the growth activity of the formation of GNP (Awadallah et al. 2017). Graphene growth activity on the Ni surface is difficult to control because carbon is soluble in nickel (Avouris and Dimitrakopoulos 2012).

The chemical vapour deposition process involved expensive and carcinogenic transition metals and high temperature processes, which are hazardous to the person in charge of the process. Also, film thickness is difficult to be controlled by this technique; yet, a limit is applied on its application on an industrial scale (Galpaya 2015). Therefore, alternative ways to functionalise and exfoliate graphite to graphene sheets are being studied further.

3.1.2 Organic chemistry reaction

The bottom-up approach through an organic chemistry reaction includes known organic chemistry mechanisms between carbon-based species. In this reaction, the active site on one species will form an interaction with an active site of another species through an organic mechanism and joins the two species through the chemical bond formed. The growth of the GO nanosheet (GON) can be controlled through controlling the processing temperature (Tang et al. 2012a). In 2012a, Tang et al. used glucose, sugar and fructose as reagents to grow GONs using a hydrothermal method. When the temperature varied between 165°C and 185°C , the thickness of the GON increased from 4.1 nm to 142 nm. A 1500 nm GO nanosheet was produced in 660 min at 180°C . Controlling the temperature during the preparation of graphene through a combination of CVD and an organic chemistry reaction is also important to produce high quality graphene (Jiang et al. 2013). Elevated temperature during the CVD process is used to avoid the absorption of elements other than the graphene film on the metal catalyst surface (Jiang et al. 2013). Byun and Coskun (2015) synthesised a 3D nanoporous graphene nanoribbon through Diels-Alders' and cycloaddition reactions between the dicyclopentadienone and arylacetylene derivatives. The approach resulted in a graphene nanoribbon with high thermal stability up to 400°C in air, high affinity for hydrogen gas (H_2), CO_2 , and methane gas and small pores that are suitable for gas filter and gas storage applications.

Even though the bottom-up approach has not been widely applied in graphene formation, it has many

advantages compared to the top-down approach. Precise graphene nanoribbon framework (GNF) with different topologies and widths are reported to be needed in applying the bottom-up approach in making GNF (Byun and Coskun 2015). Besides, the direct interaction between carbon precursors make it feasible to control the edge shape and widths on GNF (Byun and Coskun 2015). For example, a long graphene can be formed through unzipping the CNT and the graphene can further oxidised to form a GO nanoribbon (GONR) (Huang et al. 2017). The use of a small molecule and a polymer has not limited the size of the graphene produced, as a large graphene film was reported to be produced from small molecules and polymers (Jiang et al. 2013). The difficult part of the bottom-up approach is the placement of the device structure (Tour 2013). For example, it is impossible to place 1000 layers of nano-sized graphene sheets with precise location onto the intended chip (Tour 2013). Therefore, an alternative approach in graphene production was further explored. In addition, making the structure following the size region for the attachment on the electrode is difficult to obtain (Tour 2013).

3.2 Top-down graphene synthesis technique

In the top-down process, graphite or a derivative of graphite undergo an exfoliation process to separate the aggregated graphene layers to produce graphene sheets (Figure 4) (Jacobberger et al. 2015). Meanwhile, the formation of graphene from GO is done through the reduction of GO. Even though the process is slow, it is suitable for large scale production in graphene nanocomposites especially in polymer composite applications (Shah et al. 2015).

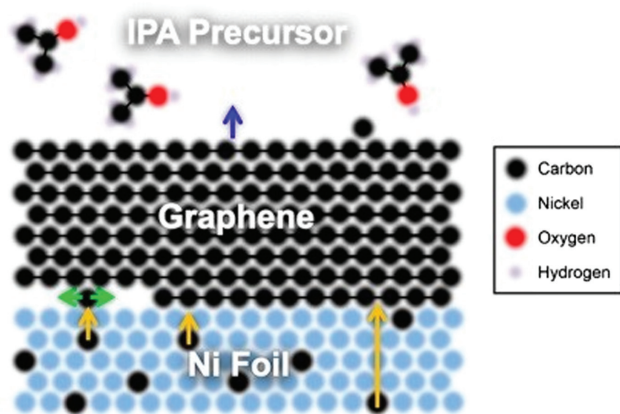


Figure 4: Process in proposed exfoliation of graphene through top down reaction. Reprinted (adapted) with permission from (Jacobberger et al. 2015). Copyright (2015) American Chemical Society.

3.2.1 Reduction of graphene oxide

Graphene production can be utilised from the reduction of GO. The discovery of methods to reduce GO is an advantageous situation for industries as it offers mass production of graphene at a low cost and high yield without disturbing the properties of the pristine graphene (Toh et al. 2014). Later in this section, three of the usual methods used to reduce GO are discussed.

3.2.1.1 Chemical reduction

Reduced GO (rGO) and pristine graphene have similarities on the structure and the arrangement of the components with both having available sp^2 hybridised carbon with delocalised π electrons (Potts et al. 2011). The chemical reduction of GO is the process of reducing GO to form pristine graphene. The difference between rGO and pristine graphene indicate that rGO contains a partly oxygenated functional group which is not reduced, while the pristine graphene component is solely formed by bonded carbon atoms. Therefore, rGO is normally used as a filler in polymer composites due to the possible hydrophilic interaction with the polymer matrix (Tang et al. 2016a,b).

The conditions and the reducing agent used determined the degree of reduction and the remaining oxygen functional group was studied from Raman spectra. The chosen reducing agent must not show reactivity with other solvent or chemicals present to ensure the reduction process is purely from the reducing agent. A strong reducing agent such as hydrazine monohydrate does not show reactivity with water, therefore it is always an option to reduce GO in an aqueous solution (Potts et al. 2011). Reduction of GO by using hydrazine or chemically reduced graphite oxide (CRGO) was highly dispersed and exfoliated in an epoxy matrix and resulted in increased mechanical, thermal stability and electrical conductivity of the composite (Gong et al. 2015). The longer the duration for the reduction treatment of graphite oxide using hydrazine is, the more oxygen functional groups are removed from the graphite surface. Besides enhancement in mechanical, thermal and electrical properties, graphite oxides that undergo 48 h of reduction treatment show photocatalyst ability to mineralise a wide range of dyes in water system (Wong et al. 2015).

Hydrazine should be avoided being applied in large scale processes due to its toxic and explosive properties (Galpaya 2015). Due to this issue, green and non-toxic reducing agents have always been chosen (Tang et al. 2012b, Zaid et al. 2015, Boro and Karak 2017, Emiru and

Ayele 2017). Emiru and Ayele (2017) specifically studied the controlled synthesis, characterization and reduction of GO for large-scale production and used ascorbic acid as a convenient and non-toxic reducing agent. The rGO was confirmed by ultraviolet (UV)-visible spectroscopy when the absorption peak of GO at 226 nm was shifted to 262 nm after 30 min reaction time indicating the restored electronic conjugation within the graphene sheet. Ascorbic acid was a stronger reducing agent as the absorption peak result was comparable with 6 h treatment of hydrazine rGO (Wong et al. 2015). The degradation of the electronic transition due to the remaining oxygen functional group and the remaining sp^3 hybrid carbon leading to loss of free electrons to carry charges, further limit the intended applications (Guo et al. 2009).

3.2.1.2 Electrochemical reduction

Electrochemical reduction is a reduction of GO using a standard normal electrochemical cell at room temperature in the presence of an aqueous buffer solution (Pei and Cheng 2012). As the method can be run at room temperature and the choices of buffer solution can be controlled, the method is cost efficient, fast, simple and not harmful to environment (Toh et al. 2014). As known, the reduction of GO will produce graphene with a partially restored pristine graphene and a partially remained oxygen functional group on the structure of the graphene sheet. The remaining oxygen functional groups will be easily manipulated to new functionalities of rGO (Toh et al. 2014).

The electrochemical reduction of GO can be conducted with chemically safe aqueous solutions as the medium in the reduction process. In addition, the reduction process can be controlled by the choice of electrolyte medium and the reduction potential (Kauppila et al. 2013). The use of easily available potassium hydroxide as an electrolyte produced an rGO film with excellent electrochemical performance such as high specific capacitance and capacitance ability even after 3000 cycles (Zhang et al. 2012). Besides basic electrolytes, an organic electrolyte medium such as acetonitrile and propylene carbonate, with a combination of negative reduction potential and pH 12 produced an rGO film with the highest C/O ratio of 4.00, which is not observable in the standard chemical and electrochemical reduction of GO (Kauppila et al. 2013). Feng et al. (2016) introduced a method for the large scale production of 1D, 2D and 3D graphene material using a prepared silk fibroin/electrochemically reduced GO (SF/ERGO) composite film. The short reduction time was observed with excellent mechanical properties and electrical conductivity of the film.

3.2.1.3 Thermal reduction

In the thermal reduction process, the oxygen functional groups from the GO surface were removed by supplying heat treatment. The reduction process does not need the dispersion of GO in a solvent to retain a partially graphite structure of rGO (Cui et al. 2016). This lowered the hazard of the volatile solvent during GO reduction. Due to the preserved graphite structure, thermal reduction could be a potential in thermoelectric applications (Pop et al. 2012). Temperature is an important factor to determine the degree of reduction. Seung (2011) used X-ray diffraction (XRD) to study the interlayer distance of GO/graphene film (GP) and reported that thermal reduction started at 500°C – 1000°C with reduced oxide layers (d_{GO}). Thermal reduction of GO was conducted by Tegou et al. (2016) for sensor applications. The reduction process ranging from 90°C to 300°C took advantage of oxygen labile behaviour when it decomposes in the presence of heat. As the reaction decomposes oxygen, the oxygen concentration in the system will be extremely high at an increased temperature (Pei and Cheng 2012). Therefore, the reaction is usually carried out in a vacuum, an inert or a reducing environment to avoid the reformation of GO by etching of oxygen in the system. Kumar et al. (2016) maintained the thermal reduction temperature and studied the effect of oxygen clustering on the graphene basal plane on the structural and electrical properties of rGO structures. The experiments and atomistic calculations done by the team showed that degree of rGO depends on types of oxygen functional groups on the GO surface and oxygen clustering on the GO surface.

3.2.2 Exfoliation of graphite

3.2.2.1 Chemical exfoliation of graphite

In chemical exfoliation, the sp^2 bonding network in the graphite carbon basal plane was disrupted with an additional functional group or ion. The additional ion or functional group on the graphite plane transform the sp^2 hybridised carbon to sp^3 hybridised carbon. Alam et al. (2016) suggested that a large alkali ion is inserted between the graphite layers to exfoliate graphite (Alam et al. 2016). Another method in chemical exfoliation is the oxidation of graphite. In the modified version of Hummer's method, the graphite oxide produced will be exfoliated to graphene oxide. It combines oxidation and exfoliation of the graphite sheet through thermal treatment. Paulchamy et al. (2015) described the reaction in simple steps. In this method, the graphite flake was exfoliated in sulfuric acid (H_2SO_4) and then oxidised with potassium permanganate (KMnO_4) and sodium nitrate (NaNO_3) catalyst at below

15°C. Water was added to complete the oxidation process. Excess KMnO_4 was removed to complete the reaction by reaction with hydrogen peroxide (H_2O_2). Finally, the mixture was washed repeatedly with hydrochloric acid (HCl) and deionised water before being vacuum dried to obtain a gel-like substance.

A concern with modified Hummer's and Hummer's method is the release of toxic gasses, nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4), during the oxidation process (Marcano et al. 2010). As the modification excludes NaNO_3 , KMnO_4 increases and maintains H_2SO_4 :hydrogen peroxide (H_2O_2) ratio as 9:1 that successfully reduces the release of the toxic gas and surprisingly increases the yield of GO (Marcano et al. 2010). The improved Hummer's method was also reported to decrease processing costs and produced environmentally friendly GO (Chen et al. 2013). The idea to oxidise graphene to GO, with the incorporation of an oxygen functional group in between the stacking graphene, has triggered new ways to chemically exfoliate graphite without changing the property of graphene.

Badri et al. (2017) exfoliated raw graphite and alkali lignin as an exfoliation agent in an aqueous medium for consistent graphene exfoliation. Besides sonication, mechanical stirring was applied to help solution exfoliation. The reaction produced high quality graphene with the remaining electrical property of graphene. In addition, a tedious reaction was avoided with the reaction at room temperature and ice bath sonication occurring in shorter sonication time.

3.2.2.2 Electrochemical exfoliation of graphite

The electrochemical exfoliation method is an approach to separate layers of graphene while retaining the properties of pristine graphene (Toh et al. 2014). The addition of an aqueous electrolyte in electrochemical exfoliation will result in fast and simple reactions. Also, high quality graphene sheets will be produced compared to rGO (Galpaya 2015).

Parvez et al. (2014) prepared graphene through the exfoliation of graphite in aqueous solutions of inorganic salts. In this study, sulphate (SO_4^-) anions offered efficiency in exfoliate graphite. An optimum condition was reported with 5 min reaction and 1.0 M SO_4^- led to 80% of 120 exfoliated graphene (EG) sheets larger than 5.0 μm , 85% abundance of thin graphene with less than three layers and ~72% abundance of bilayer graphene. Shang et al. (2016) conducted another exfoliation process with the SO_4^- ion. The study produced a comparison of the properties of graphene flakes manufactured from liquid phase exfoliation (LPE) and electrochemical exfoliation (ECE)

of graphite. The graphite electrode was self-prepared by high pressure pressing GNPs and 0.1 M sulfuric acid as the electrolyte. From the ECE exfoliation process, one monolayer of graphene flakes was observed under transmission electron microscopy (TEM) and with a narrower size distribution from 0.6 μm to 1.2 μm . Also, the EG produced from ECE was proven to have a lower level of defects or disorder with the Raman spectroscopy result of $I_D/I_G = 0.46$ compared to higher D band intensity ($I_D/I_G = 0.89$) of EG from LPE. Liu (2017) successfully synthesised graphene through multiple electrochemical exfoliations of graphite with multiple electrolytes as the electrocatalyst for the oxygen reduction reaction. In the study, oxalic acid contributed to a faster exfoliation process, better solubility of EG in deionised water and easier post-treatment of the EG and offered optimum conditions for the graphite exfoliation process.

4 Graphene reinforced polymer nanocomposite

Graphene, a nano-sized material, is an advanced filler compared to other fillers as it offers greater changes in the composites' properties with very small incorporation in the composite due to the ultrahigh aspect ratio to the matrix (Phiri et al. 2017). Manipulation of graphene derivatives and processing techniques had led to the continuous research in incorporating graphene as a reinforcement filler in polymer composites. In many studies on graphene, it has been proven that the combination of graphene and polymer properties had produced polymer nanocomposites with outstanding mechanical, thermal, electrical (Hu et al. 2014), electronic (Rozhkov et al. 2016) and optical properties (Loh et al. 2010). The excellent resultant properties of composite-filled graphene had sparked the interest of researchers to explore graphene functions in polymer composites to be used in a wide range of applications including as structural materials (Potts et al. 2011), in the automotive (Elmarakbi and Azoti 2015), medical (Pal et al. 2017), electronics (Ye and Feng 2014), gas filter (Cui et al. 2016, Ren et al. 2017), aerospace industries (Kuzhir et al. 2013) and others.

The properties of nanocomposites rely on the interaction between the filler and the polymer. The properties of composite materials improves significantly at very low loading of graphene inclusions, thus being an advanced filler as compared to other fillers (Phiri et al. 2017). This is due to the nanoscale graphene filler that offers a large surface area to volume ratio in the polymer

matrix compared to macro and micro scale fillers (Salavagione et al. 2011). A high performance polymer/graphene nanocomposite can be obtained by controlling the graphene disparity and its bonding with the polymer matrix. Thus, the ratio of graphene to polymer and the selection of graphene functionalities plays an important role (Phiri et al. 2017). However, there is a reason to consider which graphene can re-agglomerate after high exfoliation. Re-agglomeration occurs when the EG sheets regain the Van der Waals interaction. An effective processing method needs to be considered to prevent re-agglomeration of graphene (Shen et al. 2010). Therefore, to consider good interaction between the filler and the polymer matrix, the fabrication method and process to mix graphene filler and polymer matrix should also be taken into consideration to produce a high performance of composite product and to minimise the energy and cost of the production.

5 Nanocomposite processing method

To date, there are three main processing methods to initiate the interaction between graphene and a polymer matrix, which are melt mixing, solution mixing and *in situ* polymerisation. The mentioned methods will be briefly discussed in the next section.

5.1 Melt mixing

In the melt mixing method, graphene is added to a molten polymer matrix without the requirement of a solvent (Phiri et al. 2017). A good interaction between the filler and the matrix can be achieved by dispersing the filler into the matrix with sheer mixing at high temperature (Huang et al. 2012, Phiri et al. 2017). The method is suitable for industrial practices as its low cost and quick process (Papageorgiou et al. 2015). Some examples of the composites produced by this method include graphene/nanosheet polyester nanocomposites (Qiu et al. 2016), graphene/polyethylene terephthalate nanocomposites (Zhang et al. 2010), polylactide-nanographite platelets/biopolymer composites (Narimissa et al. 2014), and high density rGO/polyethylene (HDPE) nanocomposites (Woh 2015). Due to the high temperature conditions, it is useful to apply low resistant material such as a thermoplastic (Phiri et al. 2017). However, high temperatures can expose graphene to degradation (Papageorgiou et al. 2015). Besides, as the method is solvent free, high graphene

incorporation will lead to high viscosity of the graphene polymer mixture, thus limiting the dispersion of the graphene filler. In addition, high shear force can overcome graphene's poor ability to disperse and assist in its distribution into the matrix but at the cost of graphene sheet fragmentation (Papageorgiou et al. 2015). Thus, it is advisable to apply the optimum temperature and shear force during the mixing process.

5.2 Solution mixing

The solution mixing method is a simple and potential approach for large scale graphene nanocomposite production (Papageorgiou et al. 2015, Phiri et al. 2017). In this method, the polymer and graphene separately disperse in the same type of solvent before both the filler and matrix are mixed together. Among the normally used organic solvents are tetrahydrofuran (THF), toluene, dimethylformamide (DMF), and chloroform (Kaveh et al. 2014). In 2011, Verdejo et al. suggested producing graphene layers using a three-step process. First, exfoliation of graphite oxide into GO layers. Second, the reduction of GO to remove functional oxygen groups and recover the sp^2 carbon network. Last, rapid heat treatment to enable exfoliation and reduction of graphite oxide into rGO layers. In the synthesis of polyvinyl alcohol/graphene nanocomposite by the three-step process, GO was firstly dispersed in water, then gradually added with polyvinyl acetate (PVA) and sonicated. After the graphene filler and polymer matrix homogeneously dispersed, GO was then reduced with hydrazine and finally PVA/GO was heated to 100°C (Yang et al. 2010). To ensure the graphene sheet is fully exfoliated in the solvent, the graphene sheet must have good interaction with the solvent. One way to complete this requirement is by functionalising the graphene sheet to get support in the dispersal ability within the solvent and prevent re-agglomeration of the graphene sheet (Huang et al. 2012). During incorporation of the polymer, the graphene sheet was surrounded by polymers and forms an interaction with polymer and was freely dispersed in polymer matrix when the solvent was evaporated (Chatterjee and Chu 2016). Normally, ultrasonication is applied to maintain the exfoliation of the graphene sheet in the solvent and in the polymer matrix as graphene can easily re-agglomerate during the dispersion process (Fawaz and Mittal 2014, Phiri et al. 2017). The use of a solvent had caused drawbacks in this method as the solvent is costly and the disposal of solvent provides is bad for the environment as it is a non-biodegradable chemical (Papageorgiou et al. 2015).

5.3 *In situ* polymerization

In situ polymerization is a process that involves the mixing of a monomer with filler followed by self-polymerization of the monomer. Different to the melt mixing method, *in situ* polymerization can synthesise thermoplastic and thermoset nanocomposites (Fawaz and Mittal 2014). This reaction allows grafting of polymer on the graphene surface (Fawaz and Mittal 2014) and good graphene-polymer dispersion through the polymer grafted graphene interaction with a similar polymer matrix. Liu et al. (2012) conducted the *in situ* synthesis of a thermosetting polyimide with graphene oxide. The increased the hardness of the graphene/polyimide nanocomposite compared to the polyimide produced by the full exfoliation of GO in the polymer matrix (Liu et al. 2012). The advantages of the process include the possible strong interaction between the filler and the matrix and the excellent homogeneous dispersion of graphene in the polymer matrix (Verdejo et al. 2011). A good graphene dispersion can be obtained from sonication and rapid heating (Kaveh et al. 2014). The strong filler matrix interaction is worthy for producing nanocomposites with reinforcement in the intended physical and mechanical properties (Kaveh et al. 2014). This is due to the behaviour of the polymer on the graphene sheet as stress is transferred to the polymer matrix during impact (Papageorgiou et al. 2015). Functionalization of graphene sheet with a poly(p-phenylene benzobisoxazole) (PBO) monomer and further grafting with a terephthalic acid (TPA) monomer through *the in situ* process formed a strong interaction with the polymer matrix (Wang et al. 2017). However, the *in situ* synthesis is not advisable to produce nanocomposite with improved electrical conductivity as it will reduce the available sp^2 hybridised graphene sheet when graphene forms a direct interaction with the polymer matrix (Papageorgiou et al. 2015).

6 Method of designing a graphene-filled thermoset polymer

The structure of polymers such as polyesters, polyamide and polystyrene render carboalkoxy, amide and benzene ring functional groups, respectively. The structure of graphene with its hydrophobic nature is incompatible to form an interaction with the polymers (Ljubic et al. 2015). Therefore, the polar polymers with active functional groups except polymers with aromatic rings are unable to interact efficiently with nonpolar graphene (Salavagione

et al. 2011). Modification of graphene allows compatibility of graphene with the polymer matrix via non-covalent and covalent interactions is important to prevent re-aggregation during exfoliation of the filler in the polymer matrix (Ljubic et al. 2015). In later sections, examples on possible grafting of GO through covalent interactions with polymers to introduce interaction sites with the polymer matrix and examples of graphene/polymer nanocomposites are discussed.

6.1 Grafted graphene oxide

Functionalisation through the introduction of new chemical groups on graphene or GO surfaces is the best way to attain a significant performance of graphene (Liu et al. 2012, Georgakilas et al. 2016). The new chemical groups initiate interfacial interactions between the polymer matrix in composite with graphene-based materials as the mechanical integrity of the nanocomposite and their mechanical achievements (Hu et al. 2014). There are two possible processes to design functionalised GO (fGO), first through GO surface absorption or reaction with small molecules such as silane coupling agents and second through a chemical interaction between the functional groups on the GO surface with polymeric moieties (Pour and Ghaemy 2016).

During the process of absorption of small molecules in GO, small molecules acts as connectors between GO and polymer molecules. The interfacial interaction relies on coupling agent bonding with functional groups on GO. It will weaken the interaction between graphene sheets, increase its interlayer spacing, and facilitate the exfoliation and dispersion of grafted graphene by mechanical or thermal methods (Potts et al. 2011). The interlayer spacing calculated from the d -spacing value of GO was observed in the range of 0.75 nm–0.90 nm (Guo et al. 2009, Bora et al. 2013, Park et al. 2014). The importance of the bigger d -spacing value is for the dispersion of grafted graphene in the polymer matrix. Besides, ample space is also needed to further graft the GO sheets with the desired polymer molecules. An example of aliphatic coupling agent such as ATBN in Figure 5 widens the GO spacing by 14%, which is in a lower increment compared to the aromatic coupling agent (Pour and Ghaemy 2016). This is expected due to the rigidity of the aromatic structure compared to the aliphatic chain. However, the similar polarity of the aromatic ring in the GO structure and the coupling agent facilitated the aggregation of the grafted GO due to strong Van der Waals' interactions between the two molecules (Pour and Ghaemy 2016). Therefore, to avoid aggregation, a longer

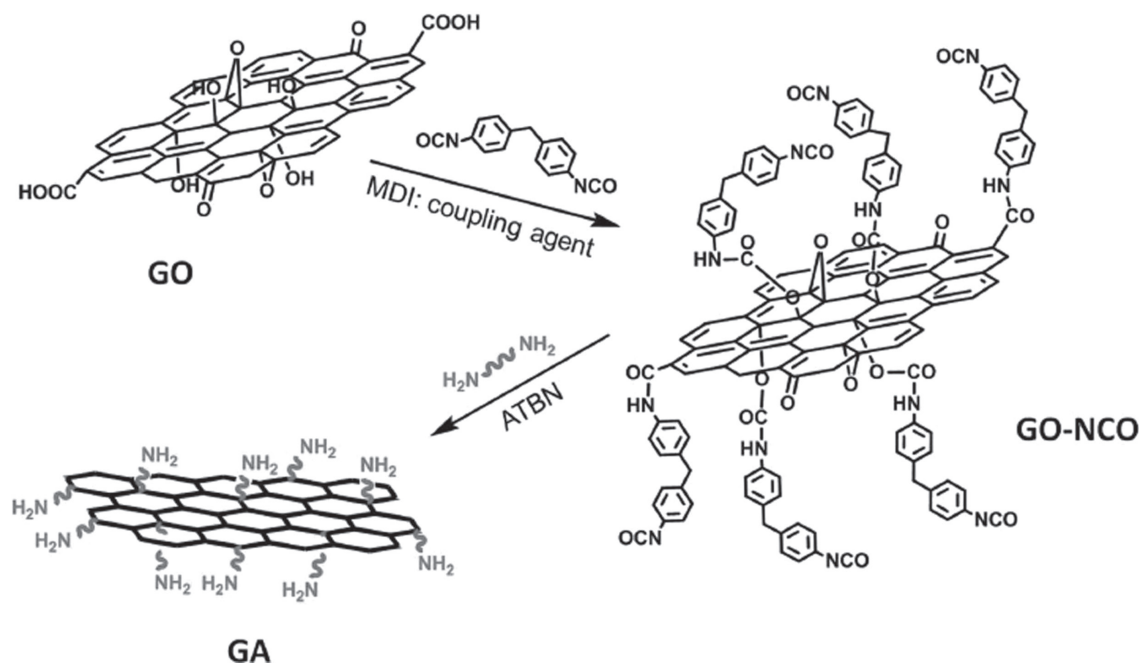


Figure 5: Schematic diagram of formation of graphene terminated with amine-terminated poly(butadiene-acrylonitrile) (ATBN). Reproduced from (Park et al. 2015) with permission from John Wiley & Sons.

aliphatic chain connected to the graphene aromatic ring is suggested.

Another method to functionalise GO is through a direct grafting of GO with a polymer. In this method, the GO surface with multiple functional groups is covalently bonded to the desired polymer. The selection of the polymer is broad and dependent on the desired properties of the polymer-grafted nanomaterials (Pour and Ghaemy 2016). GO can be grafted with poly(vinyl imidazole) chains (Figure 6). The multiple steps of synthesis and reduction of chemicals used can be avoided compared to previous methods as absorption of the small molecule on GO surface was skipped. However, this method is not eco-friendly as large volumes of solvent are needed to wash the unreacted graphitic structure and reactants after the polymerization process and during the dispersion of the polymer-grafted GO in the polymer host matrix (Sainsbury et al. 2017).

The grafting of GO with a polymer of the same functional groups to a polymer matrix leads to significant improvement in the mechanical properties of the composite. Sainsbury et al. (2017) studied covalently functionalised GO filler with poly (bisphenol A-co-epichlorohydrin) (PBE) through the interaction with the carboxylic acid group and formed an ester. The epoxy polymer grafted on GO and epoxy matrix contribute to compatibility and interfacial interaction between the two components and resulted in a 183% increase in strain to

failure of the nanocomposite compared to PBE with a GO loading less than 1 wt%.

Besides the need of the same type of polymer grafted on GO and the polymer matrix, the good interfacial interaction between the fillers and the polymer matrix can be introduced through the use of a branched polymer grafted on GO. Wang et al. (2017) designed a hyperbranched poly-ether epoxy grafted GO (GO-HE) and dispersed the GO fillers in benzoazine. TEM images showed good dispersion of 0.05 wt% (GO-HE) and an increase of 139% impact strength of the benzoazine composite.

6.2 Covalent interaction in a graphene/thermoset nanocomposite

The improvement of the mechanical properties of graphene composites relies on the interface interaction between graphene and the polymer matrix. One way to get a good interaction of graphene and the polymer matrix is through the covalent functionalisation of GO. It provides a stronger bond and interaction between GO and the polymer matrix (Ramezanzadeh et al. 2015). The covalent interaction between graphene and the polymer matrix arises from the chemical bond between the active functional groups on both graphene and the polymer surface. For example, functionalised graphene (FG) with alcohol allows the covalent attachment of the FG nanofiller and

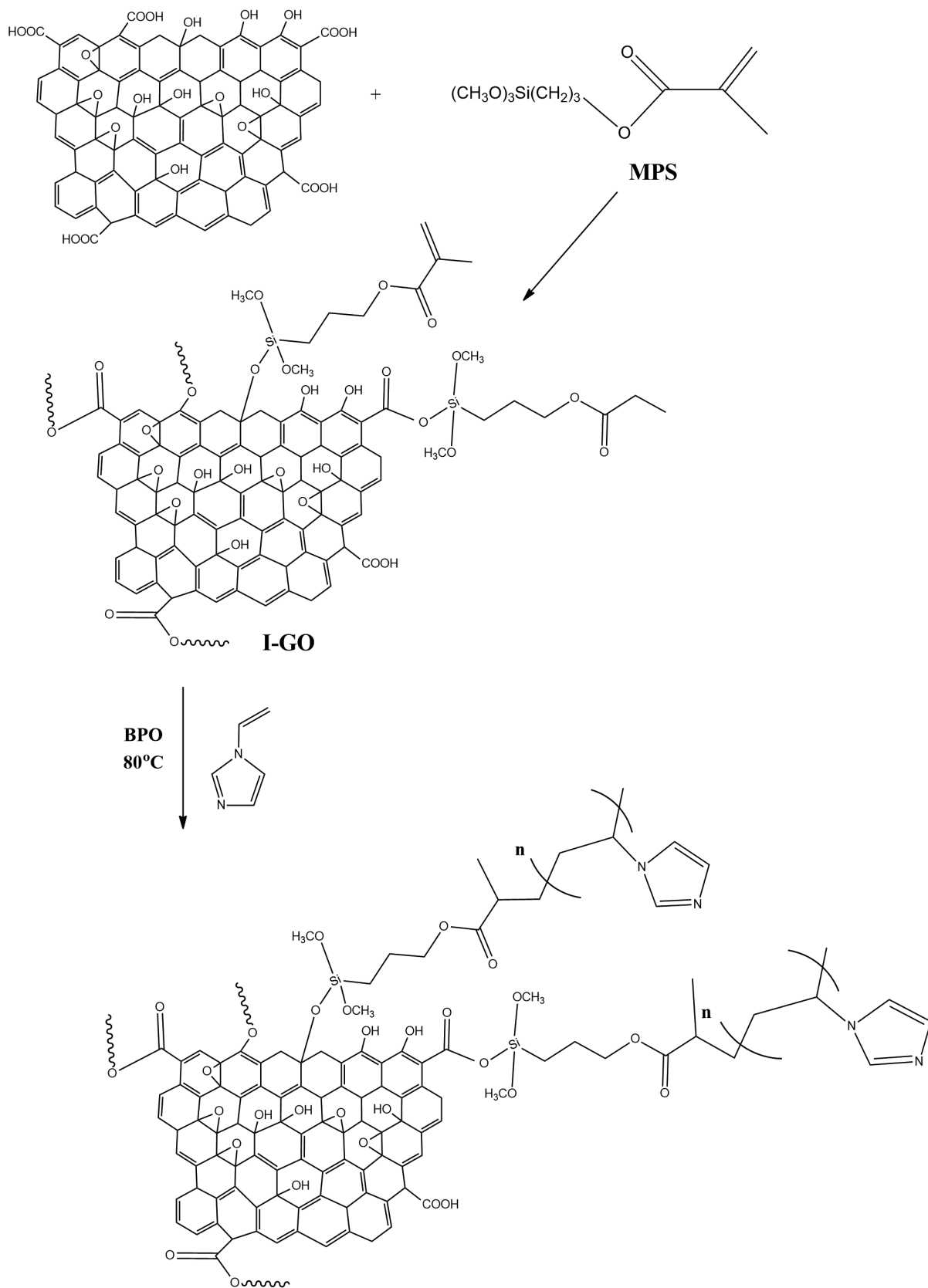


Figure 6: Schematic diagram of functionalised GO sheet with PVI chain and curing with TETA. Reproduced from (Pour and Ghaemy 2016) with permission from Elsevier.

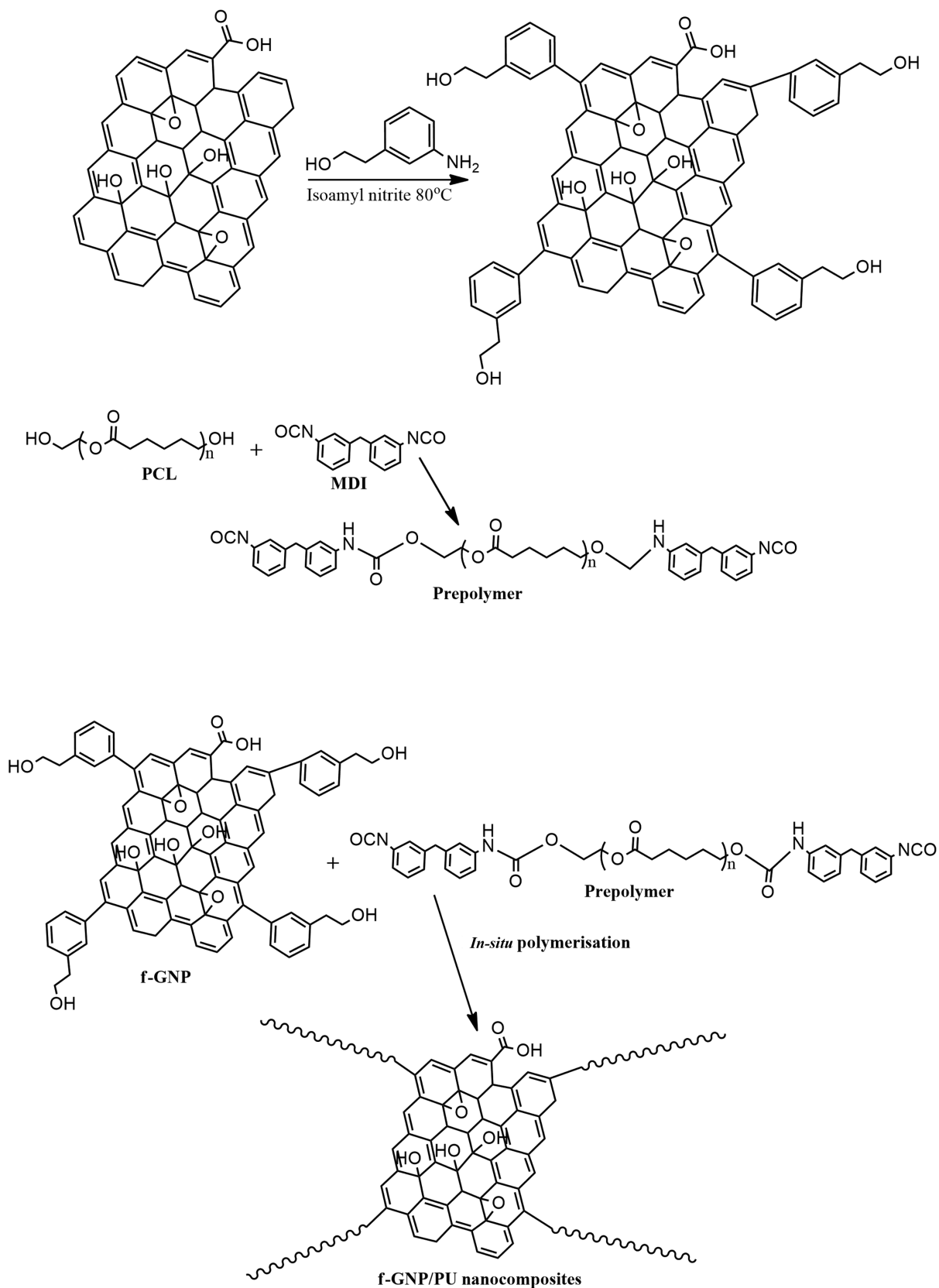


Figure 7: Schematic diagram of formation of process forming functionalised GNP/PU nanocomposite. Reproduced from (Yadav and Cho 2013) with permission from Elsevier.

polyurethane polymers matrix and forms a strong interfacial interaction between the two components (Figure 7); thus improving the interaction between the filler and the polymer matrix (Yadav and Cho 2013). In another study, PU prepolymer designed on the GO nanosheet forms an amide linkage through covalent bonding of carboxylic acid on GO and amine on methylenediphenyl diisocyanate (MDI) (Figure 8) (Li et al. 2013). The covalent interaction between graphene and the polymer matrix is not limited to the oxygen functional groups. Zhang et al. (2016) grew polyurethane/epoxy resin (PU/EP) on the 3-amino triethoxysilane FG (Figure 9) and observed finely dispersed FG in PU/EP with covalent interactions between the filler and the matrix in a scanning electron microscopy (SEM) image (Figure 10) with the appearance of a smooth silk-like wrinkle texture, which is the normal characteristic of a single layer GO (Zhang et al. 2012). The covalent interaction also leads to a polymer composite with enhanced modulus, tensile strength and elongation at the break (Zhang et al. 2012, Ramezanzadeh et al. 2015). Besides, the entanglement between the polymer will lower interfacial tension and offer improved adhesion in the matrix (Jyoti et al. 2018). From a study conducted by Jyoti et al. (2018), graphene functionalised CNT (GCNT) has a higher value of

entanglement due to the physical interaction between GO and CNT and bonding between GCNT and the acrylonitrile butadiene styrene (ABN) matrix to form a composite. As a result, the ultimate tensile strength (UTS) value of the GCNT-ABN composite increased by 22.8% and the Young's modulus increased by 105.6% with 10 wt% of GCNT compared to neat ABN.

Even though FG can perform good dispersion in a polymer matrix, the high viscosity of polymers such as epoxy and polyurethane limits the ability of graphene to start chemical interaction with the polymer. Therefore, an aid in processing FG with polymer matrix is needed. Multiple processing strategies such as ultrasonic agitation, high pressure processors and three-roll milling homogeneously dispersed the FG within the epoxy matrix (Chatterjee et al. 2012). TEM images in Figure 11A and B show the dispersion that are more homogeneous after three-mills calendaring and resulted in the homogeneous filler matrix in the nanocomposite as shown in Figure 11C. Dispersed graphene in the polymer matrix is prone to aggregate if the interfacial interaction between graphene and the polymer matrix is weaker than the Van Der Waals' interaction between the graphene sheets. A strong covalent bond between the two entities can

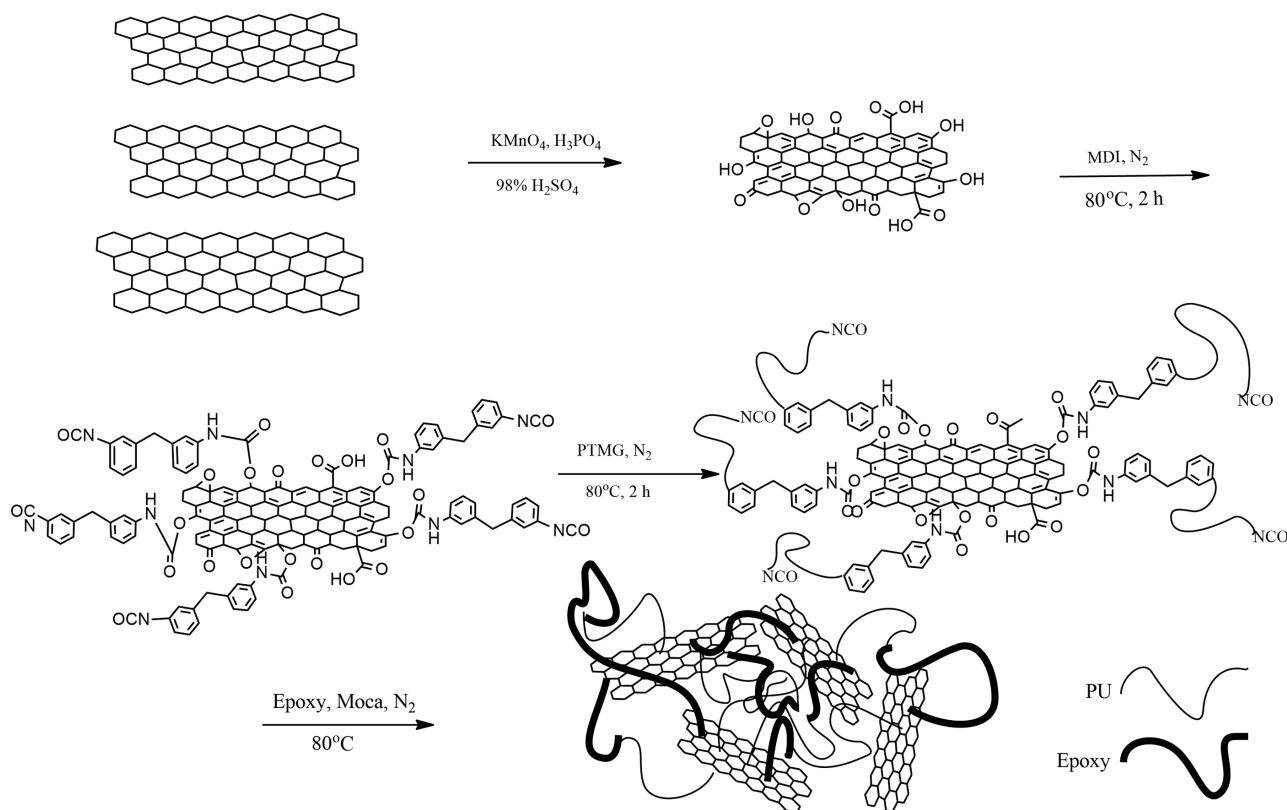


Figure 8: Schematic diagram of functionalised GO with amine and formation of polyurethane (PU)/GO/epoxy nanocomposite. Reproduced from (Li et al. 2013) with permission from Elsevier.

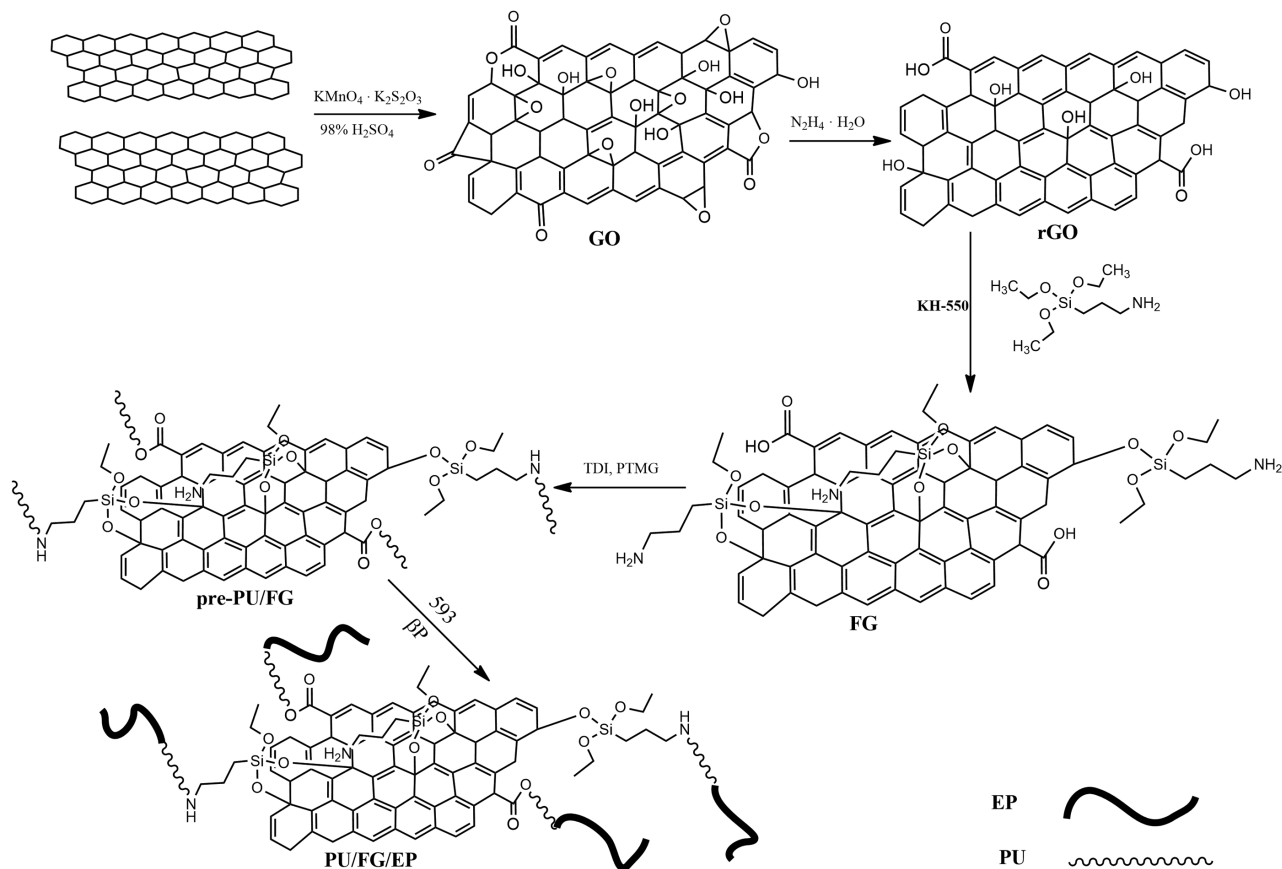


Figure 9: Schematic diagram of functionalise reduced GO with 3-aminopropyl triethoxysilane and formation of PU/FG/EP nanocomposite. Reproduced from (Zhang et al. 2016) with permission from Elsevier.

prevent aggregation. Cai et al. (2012) prepared amine functionalised graphene and introduced a -NH-CO- covalent interface with the PU matrix. A good dispersion of GO in the PU matrix is observed from the SEM image in Figure 12B compared to Figure 12A with the average thickness of the GO strip being less than 50 nm. The well-dispersed GO in the PU matrix results in 700% increment in Young's modulus and an approximate 50°C increment in decomposition temperature with 4% GO loadings. In addition, decoration of acrylates on the GO surface for interfacial interactions with poly(methyl methacrylate) matrix not only enhanced the mechanical properties but also produced a composite with outstanding stress transfer between FG and the polymer matrix (Gong et al. 2016).

6.3 Non-covalent interaction in a graphene/thermoset composite

Non-covalent interaction is an intermolecular interaction between two molecules. In the graphene/thermoset

composite, non-covalent interaction occurs when both the graphene and the polymer have no functional groups that can form chemical interactions. Even so, the non-covalent interaction is useful to make sure graphene had dispersed in polymer matrix. Tang et al. (2013) found that different dispersion routes with and without a ball mill procedure caused different dispersion levels of graphene, thus had a different effect on the mechanical properties of graphene/epoxy composites. Mixing of 0.2% rGO with epoxy by sonication and by the planetary ball mill led to 52% of fracture toughness compared to 24% fracture toughness when rGO/epoxy was mixed by sonication only. The dispersion of a higher concentration of graphene through the ball milling process was reported to produce composites with improved mechanical properties and high electrical conductivity (Xu et al. 2016). In a study conducted by Bora et al. (2013), a good dispersion and strong interfacial interaction of rGO in the PE matrix as seen in Figure 13 was achieved when rGO initially was dispersed in THF followed by vigorous mechanical stirring of the PE/rGO mixture. The simple and straightforward method resulted in a 123%

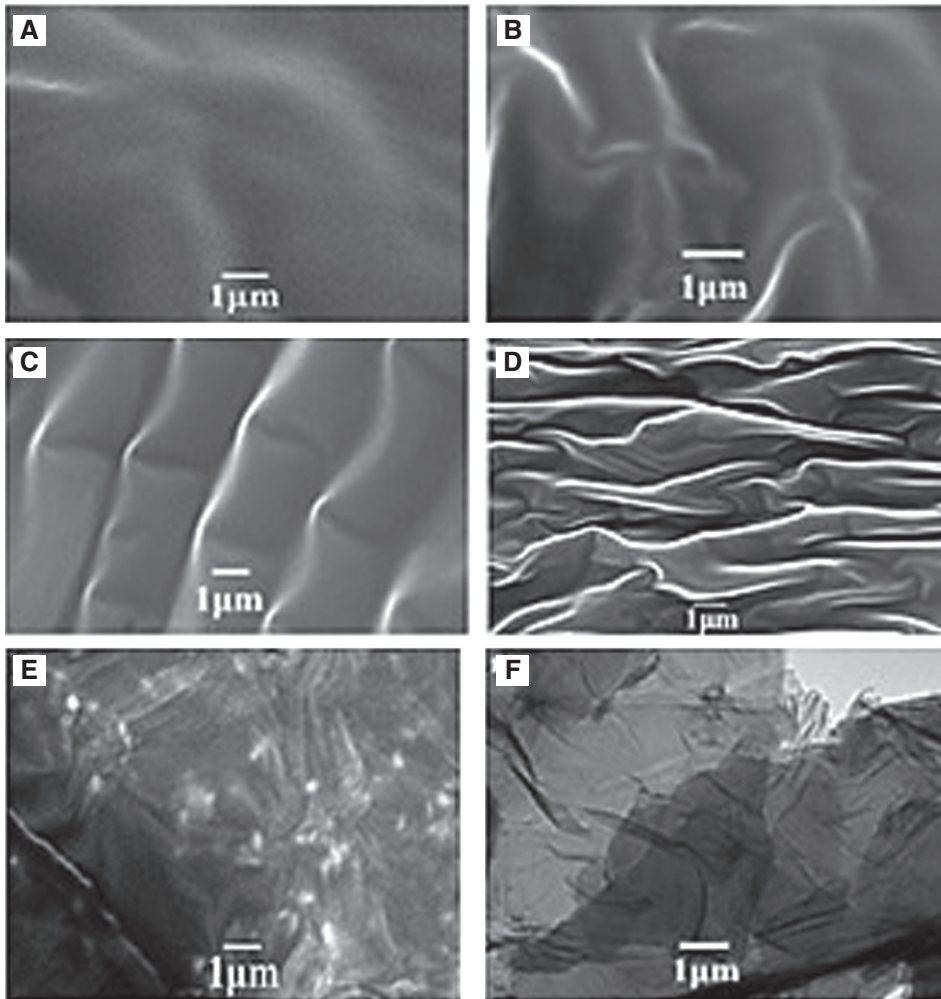


Figure 10: SEM images of fractured surface of composites at different PGE loading.

SEM images of the fractured surfaces of the (A) PU/FG/EP: PU/EP, (B) PGE-0.5, (C) PGE-0.8, (D) PGE-1.0, (E) PGE-1.5, (F) and TEM images of FG. Reproduced from (Zhang et al. 2016) with permission from Elsevier.

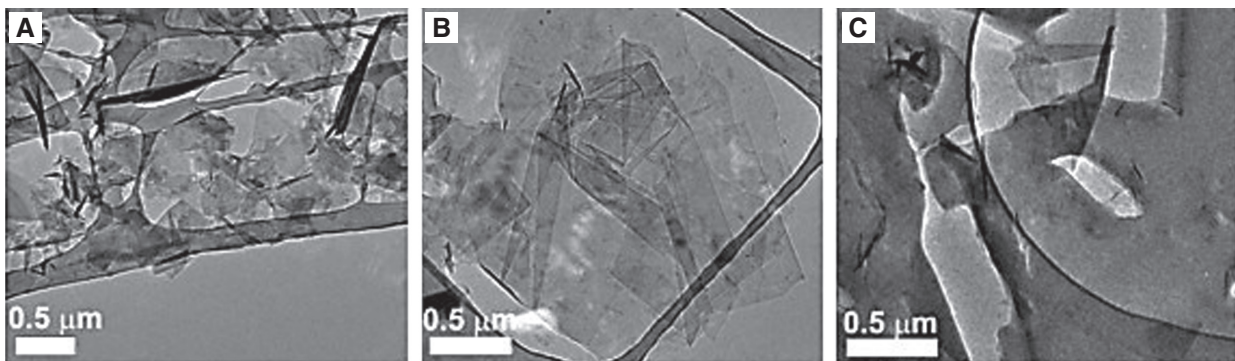


Figure 11: The figure shows SEM images of graphene dispersion homogeneity through different processing techniques.

SEM images of dispersion of EGNP in amine (A) after high pressure homogenization (B) after calendaring and (C) 0.5% in the final epoxy composite. Reproduced from (Chatterjee et al. 2012) with permission from Elsevier.

increase in the tensile strength and an 87% increase in the Young's modulus with 3% rGO. Le and Huang (2015) had reinforced an epoxy/polyester resin with a GNP by using a

high intensity ultrasonicator for the homogeneous mixing of the polymer resin and GNP and removed trapped air in the composite using a high vacuum. With an optimum

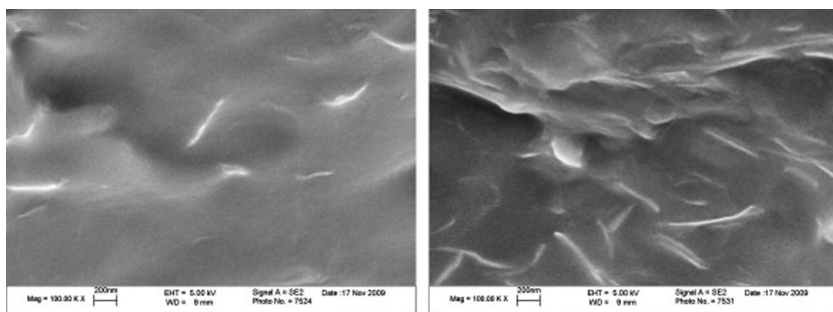


Figure 12: SEM images of GO/PU nanocomposite indicating average thickness of graphene – nanoflakes. PU matrix represented by the dark area. The bright strips are graphene-nanoflakes with thickness 30–50 nm. Reproduced from (Cai et al. 2012) with permission from Elsevier.

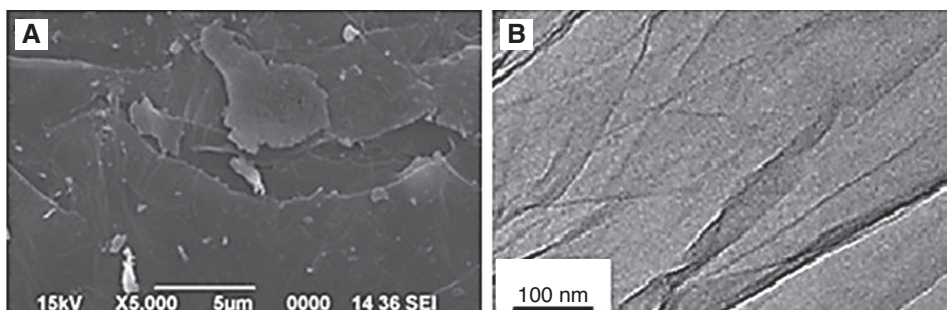


Figure 13: SEM image of dispersion of GO at different GO loading. Part (A) neat PE (B) GO/polyester with 3% GO. Reproduced from (Bora et al. 2013) with permission from Wiley & Sons.

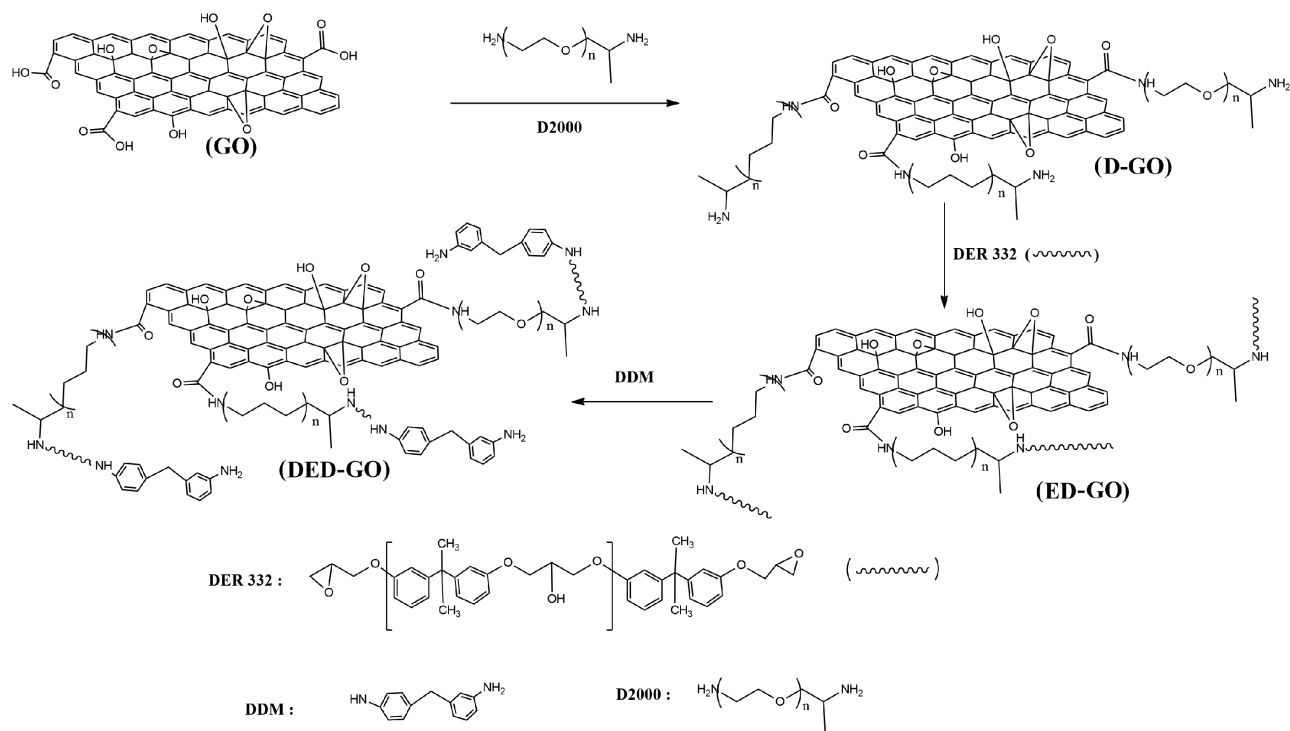


Figure 14: Schematic diagram of three steps surface modified GO. Reproduced from (Liu et al. 2014) with permission from Elsevier.

loading of 0.2% GNP, the tensile stress of the nanocomposite rose by 86.8% compared to the epoxy/PE resin.

Besides processing techniques, functionalised GO (fGO) with polymers can assist the dispersion of graphene and prevent aggregations. Besides, the improved mechanical properties of the composites is due to the interaction between functional groups on the graphene surface with the polymer matrix. Liu et al. (2014) prepared nanocomposites with grafted GO nanofiller through the three steps of GO grafting as shown in Figure 14. The hydrogen bond interaction between DED-GO and epoxy acted as a bridge to equally disperse stress onto the GO nanosheet and linked the epoxy molecules, thus strengthening the composites. As a result, the tensile strength and the storage modulus of the epoxy nanocomposite were increased by 30% and 62%, respectively, with the incorporation of only 0.2 wt% fGO. In addition, elongation at break was also increased at the same GO concentration, which was not observed in the study conducted by Bora et al. (2013). For a rGO system, residual functional groups on the rGO surface are the factors for thermal conductivities stability of the composite. Sun et al. (2016) reported an epoxy resin with rGO processed over a longer period resulted in the decrease of the thermal conductivity of the composite. This is due to less functional groups on rGO and it suppressed the ability of the filler to make an interaction with the epoxy matrix.

7 Graphene derivatives reinforced an epoxy polymer

Epoxy resin is one class of thermoset materials found during the late 1930s (Svendsen 2014). They are well applied in composite applications due to their being chemically compatible with most substrates. However, its natural stiff property had gained researchers attention to improve its mechanical performance. Graphene is one of the nano-additives that can be added to epoxy resins for improved mechanical properties of the composite. For example, GNPs and ionic liquid were added to an epoxy to add flexible behaviour to the epoxy composite (Hameed et al. 2018). The π - π stacking interaction between ionic liquids on the graphene surface and the epoxy induce high level of dispersion of the platelet in the epoxy matrix. As a result, the addition of a small concentration of graphene of 0.6 wt% increased the tensile strength and Young's modulus by 125% and 21%, respectively (Hameed et al. 2018). In addition to the non-covalent interactions, surfactant treatment of thermally reduced GO (TRGO) and graphene in an epoxy

matrix improved the interface interaction and the mechanical properties of the epoxy composite with a small loading of graphene (Wan et al. 2013, Zang et al. 2015).

Functionalisation of graphene allows a stronger interaction with the epoxy matrix to facilitate the dispersion through a chemical interaction. In a comparison study of epoxy/GNP and epoxy/graphene functionalised composite conducted by Berhanuddin et al. (2017), the functionalisation resulted in the interface interaction between the epoxy and the FG and led to improved mechanical properties of the composite. Among the molecules to functionalise GO, the molecules with epoxy functional groups are a good choice to produce composites with higher increment in the Young's modulus and the tensile strength of epoxy/FG compared to epoxy/graphene composites (Wan et al. 2013, 2014) and thermal properties (Wan et al. 2013). In addition to the specific type of polymer used to functionalise GO, the length of the polymer was also important to produce a composite with the desired properties (Guan et al. 2014). Guan et al. (2014) concluded that GO functionalised with a shorter polymer will produce significant improvements in composite strength but small improvement in ductility and toughness of the composite compared to GO functionalised with a longer polymer.

Most commonly, graphene was oxidised to GO to introduce oxygen functional groups on the graphene surface. The same polarity of oxygen functional groups on the graphene surface with epoxy in the epoxy polymer matrix allows an interphase interaction between GO fillers and the epoxy matrix. Adak et al. (2018) studied the mechanical property of a fibre/GO/epoxy composite as GO is a sandwich layer that connect the epoxy and the carbon fibre 2D structure. They claimed that the interfacial interaction between the fibre and the matrix increases with the addition of GO particles and leads to an increase in the tensile strength by 34% at 0.2 wt% GO. The theory was supported by Pathak et al. (2016) when 0.3 wt% GO was applied to the sandwich composite it resulted in an increase in the bending strength and modulus by 66% and 70%, respectively. In addition, Pathak et al. (2016) measured the interfacial interaction between the two components through interlaminar shear strength (ILSS). The strong interfacial interaction was proven by Pathak et al. (2016) when the ILSS of the composite increased by 25% at only 0.3 wt% incorporation of GO. However, the increment in ILSS is lower than that observed by Yao et al. (2018) with an increase of ILSS of the composite system by 58.6%. In the system, multiple possible interactions such as epoxy/carbon fibre interaction and epoxy/hardener interaction may contribute to the increase in ILSS. Another study done by Alexopoulos et al. (2017) supports

the contribution of GO/epoxy interaction in increasing the epoxy's mechanical property. The tensile strength of the GO/epoxy composite with 0.25 wt% of bigger particle diameter (15 μm) of GO showed an increment of 17.1% tensile strength compared to an increment of 11.3% tensile strength of smaller GO particle diameter (2 μm) with the same concentration. This shows the bigger the size of graphene oxide, the more interfacial interaction between GO and epoxy matrix occurs, thus leading to an increased tensile strength of the epoxy composite. Unfortunately, an increase in the amount of GO to 5.0 wt% led to the weaker mechanical strength of the composite due to the agglomeration of GO.

In addition to GO with oxygen functional groups grafted graphene, graphene and GO can be further functionalised to facilitate the dispersion of FG in an epoxy matrix and can improve the mechanical properties of the epoxy. Ferreira et al. (2018) fGO with hexamethylenediamine and conducted a hardness test on the composite. High concentration of GO with 1 wt% is required for 33% increased composite hardness compared to the GO/epoxy composite. Huskić et al. (2018) reported low loading of amine fGO in an epoxy with improved mechanical properties of the material. GO was directly used in solution form after the synthesis without normal drying and was functionalised with an amine. At this stage, GO was prevented from agglomerating and was separated into individual sheets. A small concentration of NPs then dispersed in the epoxy matrix and at <1.0 wt% GO, the tensile strength of the smaller fGO particle size was not affected but an increase of $\approx 10\%$ tensile strength irrespective of GO concentration of the bigger fGO particle was obtained. The result was the same as that reported by Alexopoulos et al. (2017), which is that the bigger particle size of GO gives a better tensile strength of the epoxy/unmodified GO composite. A small concentration of fGO was able to improve the mechanical properties of the epoxy composite. Li et al. (2016) reported the impact strength of epoxy nanocomposite that contained inorganic sulfonic graphene oxide (SGO). The flexural strength and modulus started to increase with 0.25 wt%–1.0 wt% SGO. The highlight of the study was the successful cross-linking between SGO and an epoxy matrix at 1.0 wt% SGO that led to 113% increment in the impact strength. Epoxy nanocomposite incorporated with plasma fGO was reported to increase the fracture energy by 51.2% with only 0.2 wt% f GO. The result was 4-fold lower than reported by Chhetri et al. (2017) when GO was functionalised with peroxy radicals. Chhetri et al. (2017) studied the functionalisation of GO with peroxy radicals and the mechanical properties of these nanofiller epoxy composites. At 0.2 wt% fGO, bond formation between

the pi electron resulted in 28% increment in the Young's modulus, 19% increment in the tensile strength and 240% fracture energy of the nanocomposites. The increase in the fracture energy can be explained through the undisturbed sp^2 structure of graphene when functionalised with peroxy radicals lead to a load transfer throughout the graphene hexagonal structure and preserved the graphene properties.

8 Graphene reinforced a bio-based thermoset polymer

In recent years, intensive research on bio-based polymers was observed due to their low carbon footprint and possible biodegradability (Sisti et al. 2016). Besides, the search to replace petroleum-based polymers with bio-based polymers is important to diminish greenhouse gas emissions and its effect on climate change. A challenge to replace petroleum-based polymers with bio-based polymers arise with the deficiency of mechanical and thermal properties of bio-based polymers. One way to overcome the issue is by high performance graphene filled into the bio-based polymeric system. Many techniques were applied to incorporate graphene into bio-based polymers and the mechanical and thermal performance of the composite are comparable with petroleum-based composite systems.

The important factor to improve the properties of composites is graphene dispersion and its stability in the dispersion form in a period of time. Dispersion of GO in organic solvent through the solvent exchange technique conducted by Zhang et al. (2012) was reported to produce dispersed GO with single layer of GO (Zhang et al. 2012). The study on bio-based polyester (BE) grafted on rGO (Figure 15) resulted in drastically increased electrical conductivity of the composite by only 0.16 vol%, and the thermal conductivity of composites increases consistently with the increasing graphene content (Tang et al. 2012b). The thermal conductivity of the composites containing 1.45 vol % graphene increases by 185% (from 0.19 to 0.542 $\text{W m}^{-1} \text{K}^{-1}$). Homogeneous dispersion of graphene in BE matrix was concluded from SEM image in Figure 16. The parallel increasing thermal conductivity with increased graphene concentration in the composite was also reported by Cao et al. (2013). Without dispersion of graphene/epoxy mixture before curing, the thermal conductivity and electrical conductivity of the composite increased with only 0.5 vol % and 0.121 vol % loading of graphene, respectively.

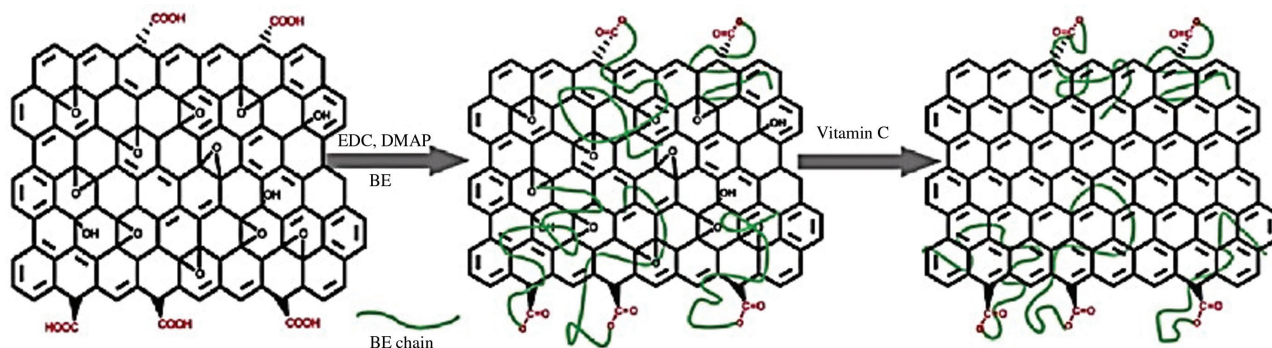


Figure 15: Schematic of synthesis of BEGO and BEG.

Reprinted (adapted) with permission from (Tang et al. 2012b). Copyright (2012) American Chemical Society.

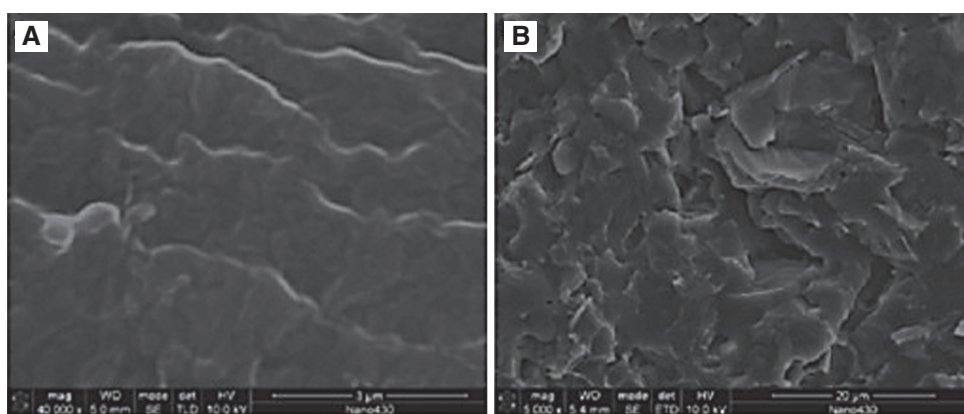


Figure 16: Cross-section SEM images of the composites with different graphene loading.

Part (A) 0.16 vol % graphene and (B) 1.06 vol % graphene. Reprinted (adapted) with permission from (Tang et al. 2012b). Copyright (2012) American Chemical Society.

Neither bio-based thermoplastic nor bio-based thermoset graphene composites can have mechanical properties as good as petroleum-based graphene composites (Sisti et al. 2016). Eksik et al. (2016) prepared nanocomposite that involved loading of the cardolite matrix and graphene platelet (GPL) as a nanofiller through solution mixing with acetone as the solvent followed by a sonication process. It was reported that Young's modulus, tensile strength and fracture toughness of the bio-epoxy resin increased by 258%, 94% and 157%, respectively, on the addition of 0.5 wt% GPL. The mechanical properties of composite were further improved with an increased interface interaction between the polymer matrix and the graphene filler. Baruah and Karak (2016) prepared hyperbranched bio-based epoxy matrix synthesised from phytochemical tannic acid (Figure 17). Hyperbranched polymer is an example of a polymer with multiple points of interaction to a graphene filler (Boro and Karak 2017). Dispersion of GO in THF before mixing with hyperbranched epoxy (HBE) conducted by Baruah and Karak (2016) led

to an increased tensile adhesion strength of the HBEGO nanocomposite by 189%, impact resistance (toughness) by 263%, tensile strength by 161% and elongation at break by 159% with 0.5 wt% GO.

The proper interaction successfully stopped crack propagation and formed a complicated direction for crack

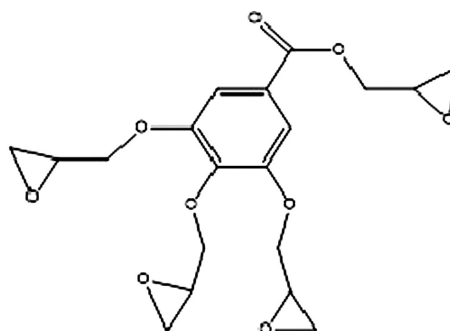


Figure 17: Gallic acid with epoxy functional groups.

Reproduced (adapted) from (Cao et al. 2013) with permission of The Royal Society of Chemistry.

Table 1: The property of TAERGO nanocomposites.

Properties	TAE ^a	PNC0.25 ^b	PNC0.50 ^c	PNC1 ^d
Tensile strength (MPa)	11.6 ± 0.3	27 ± 0.5	24 ± 0.3	27 ± 0.7
Elongation at break (%)	55 ± 3	60 ± 7	77 ± 5	105 ± 3
Scratch resistance (kg)	5 ± 0.3	7 ± 0.5	7.5 ± 0.3	8 ± 0.2
Impact resistance (cm)	55 ± 3	70 ± 5	80 ± 5	90 ± 7
Tensile adhesive strength (MPa)	227 ± 0.3	270 ± 0.5	311 ± 0.5	345 ± 0.3

^aTAE: hyperbranched epoxy.

^bPNC0.25: TAE with 0.25% RGO.

^cPNC0.5: TAE with 0.5% RGO.

^dPNC1: TAE with 1% RGO.

propagation. As a result, various enhancements in the mechanical and other properties as reported are stated in Table 1.

In addition to the various examples discussed, a comparison of different methods, variety of graphene reinforced/polymer nanocomposites and the resulting mechanical and thermal properties are summarised in Table 2.

9 Reinforced properties of a graphene/polymer nanocomposite

9.1 Mechanical properties

Mechanical properties are the most important aspect to look for in structural composites. Since the emergence of discoveries of graphene allotropes, many studies on graphene have been directed to form improved mechanical, thermal, optical, and electrical properties of nanocomposites. Intrinsic property of reinforcement and good interaction with polymer hosts are the factors for the enhanced mechanical properties of polymer nanocomposites (Fang et al. 2010). Therefore, selective reinforcement materials are essential to predict improved mechanical properties of polymer nanocomposites.

Graphene filler can prevent failure or fracture when it is able to resist propagation of an advancing crack (Atif et al. 2016). Fracture toughness of an epoxy can be improved with very low loading of graphene (Atif et al. 2016). Atif et al. (2016) also described that in a nano-system with an epoxy as a matrix and graphene as a filler, propagation of cracks through an epoxy matrix stopped by the graphene sheet causes trouble. However, to maintain the graphene position as a filler in the epoxy matrix, the crack bridging provided by graphene deepened on its dispersion state and interfacial interaction with the epoxy matrix (Atif et al. 2016).

In order to maintain a strong interfacial interaction between the graphene filler and the polymer matrix, the optimum amount of graphene is needed (Saleem et al. 2016). Low percentage by weight of graphene filler in a polymer matrix offers small points of interfacial interaction, thus resulting in weak interaction between the two elements (Ebrahimzadeh et al. 2016). The weak interaction will increase polymer chain mobility and flexibility, thus creating empty spaces between the graphene and the polymer matrix, and subsequently effective propagation of cracks occur (Ebrahimzadeh et al. 2016).

Polymer chain mobility and flexibility in nanocomposites does not only occur at low loading of graphene filler, but also at high concentration of graphene filler loading (Ebrahimzadeh et al. 2016). At high graphene loading, the nanocomposite system is exposed to re-agglomeration of graphene filler (Shah et al. 2015). The formation of staggered layers of graphene will reduce the interaction between the graphene filler and the polymer matrix. A highly concentrated graphene environment induces interaction between graphene layers due to higher surface energy between graphene than the interaction between graphene and the polymer matrix (Zhang et al. 2016). The same reason was applied to low loading of graphene filler whereby a new weak point in the nanocomposite was created (Ebrahimzadeh et al. 2016). As a result, GO loading with higher than 0.5 wt% had reduced tensile strength and storage modulus of the system compared to results obtained at 0.5 wt% or higher GO loading (Shah et al. 2015). In addition, higher graphite weight loading was also reported to cause a decrease in elongation of break for composites due to agglomeration, thus weakening the interfacial bonding between the treated graphite and the polymer matrix (Rus et al. 2015).

From these examples, graphene agglomeration is among the factors for structural failure of the nanocomposites. He et al. (2017) studied very low GO derivatives in unsaturated polyester resin to toughen the nanocomposite. The reason for the re-agglomeration event of graphene

Table 2: Summary of examples of graphene/polymer nanocomposites with processing methods and reinforced mechanical properties.

Reinforcement	Modification	Method	Matrix	Remarks	Ref.
0.2 wt% rGO		Solution mixing	Epoxy	52% ↑ fracture toughness	(Tang et al. 2013)
0.5 wt% GO	Hyper branched epoxy	Solution mixing	Epoxy	189% ↑ adhesive strength 263% ↑ toughness 161% ↑ tensile strength 159% ↑ elongation at break	(Baruah and Karak 2016)
0.2 wt% GNP		<i>In situ</i>	Epoxy/polyester	31.8 MPa tensile strength 86.8% ↑ tensile strength At 1 wt% storage modulus at 30°C 3100 MPa 1 wt% thermal conductivity 33.3%	(Le and Huang 2015)
1 wt% functionalised graphene flake	1-pyrenebutyric acid	Solution mixing	Epoxy	100% ↑ storage modulus T _g increase 91.9°C–97.8°C Modulus from 458 to 657	(Song et al. 2013)
3 wt% functionalised graphene sheet		solution mixing	Polyurethane		(Nguyen et al. 2009)
GO		<i>In situ</i>	Polyallylamine	200% ↑ tensile strength 330% ↑ Young's modulus	(Satti et al. 2010)
5.3 wt% GNP		Solution mix	Styrene rubber	24% ↑ thermal conductivity 413% ↑ tensile strength 782% ↑ young modulus	(Araby et al. 2013)
0.54 v/v% graphene sheet		Solution mix	Epoxy	41% ↑ fracture toughness 25% ↑ elastic modulus 10% ↑ tensile strength	(Qiu and Wang 2011)
0.1 wt% fGO nanosheet	Isocyanate	Solution mixing	Polyurethane	23% ↑ elongation at break 47.5% ↑ modulus (72 h)	(Ramezanzadeh et al. 2015)
0.1 wt% – 0.8 wt% graphene platelets		Solution mix	Epoxy	94.1% ↑ tensile strength 258.6% ↑ young modulus	(Eksik et al. 2016)
0.9 wt% functionalised graphene nanosheet	Diazonium addition/ATRP	<i>In situ</i>	Polystyrene	69.5% ↑ tensile strength 57.2% ↑ Young's modulus 82% ↑ T _g	(Fang et al. 2015)
0.1 wt% graphene oxide 3	Phase transfer agent TGPAP	Solution mixing	Epoxy	75% ↑ fracture toughness 92% ↑ tensile strength 36.5% ↑ flexural strength – 37.7% ↑ flexural modulus	(Wang et al. 2013)
1.0 wt% GO		<i>In situ</i>	Epoxy	137% ↑ micro hardness 28% ↑ modulus Glassy moduli ↑ 30% at 50°C and 70% ↑ at 190°C	(Tang et al. 2016a,b)
5 wt% GNP		<i>In situ</i>	Epoxy		(Prolongo et al. 2013)

Table 2 (continued)

Reinforcement	Modification	Method	Matrix	Remarks	Ref.
0.5 wt% GNP		1) High Shear mixing, 2) Three roll mill, 3) High shear mixing and three roll mill Solution mixing	Epoxy	94.1 wt% ↑ storage modulus in rubbery state 5.3% ↑ degradation temperature 7% ↑ 2nd glass transition	(Prolongo et al. 2013)
0.1 wt% GO		Solution mixing	Epoxy	50% ↑ fracture toughness 0.5 wt% GO – 35% ↑ elastic modulus, 28% ↑ tensile modulus	(Galpaya et al. 2014)
0.04 wt% mGO 5 wt% GNP	TMI isocyanate	<i>In situ</i> Melt compounding	UPE Polylactic acid	55% ↑ G_c 10% ↑ Young's modulus for GNP-S 24% ↑ Young's modulus for GNP-L	(He et al. 2017) (Zhang et al. 2016)
6 wt% graphene		Solution mixing	PHBV plastic	25.71% modulus at break T_g increase to 23.9°C 67% ↑ tensile strength	(Sridhar et al. 2013) (Yuan et al. 2012)
0.5 wt% graphene nanosheet 2 wt% GO	Amide alkyl chain	<i>In situ</i> Solution mixing	PMMA PVA	92.9% ↑ tensile stress 167% ↑ solution mixing 40% ↑ tensile modulus 39.4% ↑ elastic modulus	(Yang et al. 2011) (Scaffaro et al. 2017)
5 wt% GNP		Melt compounding	PLA	14% ↑ Young's modulus 20% ↑ tensile strength 20% ↑ toughness T_g increase to 2.6°C	(Pinto et al. 2016)
0.25 wt% GNP		Melt blending	PLA	At 0.5 wt% 13% ↑ tensile strength	(Kim and Jeong 2010)
0.5 wt% exfoliated graphite		Melt compounding	PLA	at 3% wt% degradation temperature increase by 14 K 95% ↑ tensile strength 66% ↑ modulus 414% ↑ energy a break 16.4% tensile strength 126.9% Young's modulus 52% ↑ tensile strength 47% ↑ young modulus	(Wan and Chen 2011) (Surudžić et al. 2016) (Abdolmaleki et al. 2017)
0.3 wt% GNP		Solution mixing	PCL Poly(ϵ -caprolactone)		
0.01 wt%	Ag	Electrochemical reduction of Ag	PVC		
5 wt% graphene frGO	Glucose	Solution mixing	PVA		

GO, Graphene oxide; GNP, Graphene nanoplates.

is not only the fusion of high concentration of graphene to the polymer matrix, but also because of the size of graphene re-agglomerates (He et al. 2017). Highly re-staging graphene, which will form larger graphite, can cause deterioration of the composite and facilitate crack propagation (He et al. 2017). Proper graphene dispersion, which means more interfacial contact and interaction between graphene filler and the polymer matrix, is important to decrease the size of GO sheets and the size of GO agglomerates (He et al. 2017). This can be achieved through sonication, a practice that homogenises the dispersion more extensively (He et al. 2017). Sonication of fGO with isopropenyl- α,α -dimethylbenzylisocyanate (TMI) and dodecylamine (DDA) with unsaturated polyester resin produced a nanocomposite with a 12–25% increase in the toughening effect and fracture energy of 18–55% improvement with only 0.02–0.08 wt% of modified GO compared to neat UPE resin.

9.2 Thermal property

Generally, graphene has lower thermal stability than graphene nanocomposites (Fang et al. 2010, Shen et al. 2011). Thermal decomposition of a material occurs when the material fails to retain its construction. For a nanocomposite material, the system including filler and matrix must retain and resist thermal pressure to become stable at heated temperature. To maintain the nanocomposite structure, graphene filler and the polymer matrix must have strong interaction, which will control polymer chain mobility (Singh et al. 2011).

Graphene-based nanocomposites have shown better improvement in nanocomposite thermal property due to their higher surface contact area with the polymer matrix compared to multi-walled carbon nanotubes (Li et al. 2017). Close proximity interaction between the thin epoxy layer and GNP ease vibration of crystal lattice to be transported across the two materials (Li et al. 2017), and with the help of graphitic thermal conductivity offer better thermal conductance in the material. The greater the filler content or GNP lateral size, the greater will be enhancement in thermal conductivity (Li et al. 2017). However, optimum concentration of GNP loading is crucial to avoid re-agglomeration that can lead to deterioration of the mechanical properties of nanocomposites and increase in viscosity of the materials, which will lead to material processing difficulties (Li et al. 2017).

In 2009, Yang et al. studied the effect of covalent functionalization of a graphene nanosheet on the

nanocomposite thermal stability. The thermal stability of composites is indicated by the glass transition temperature (T_g), which is the relaxation behaviour of the nanocomposite system (Fang et al. 2015). The increase in T_g thus reflects the strong and close packing of the graphene sheet on the polystyrene (PS) chain to close proximities through covalent bonding. According to the study, rapid mass loss of graphite oxide started at lower temperatures (150°C vs. 200°C) due to a larger available defect density in the sample. Coated graphene on PS polymers had decreased defect density of graphene. Therefore, thermal stability was enhanced when the resulting graphene-PS sheet maximum mass lost temperature more than 100% higher than that of graphite oxide.

10 Future trends and outlook

There is no doubt that adding GO to a polymer matrix offers an increase in mechanical properties of the composite. The increase in mechanical behaviour is due to homogeneous dispersion of intercalated and interaction between grafted GO with the polymer matrix. The examples shown here are laboratory scale production of nanocomposites with a small amount of grafted GO and polymer matrix used. The success of homogeneous dispersion of grafted GO on a large scale production is unknown. Besides, dispersion of grafted GO needs a high volume of solvent. In a large scale production, a high volume of grafted GO must disperse in a vast volume of solvent at a longer time for homogeneous dispersion. The dispersion issue is one of challenges to overcome to ensure convenient methods with optimum energy consumption and the use of harmful solvents during production of graphene nanocomposite on the industrial scale.

Graphene had been extensively studied especially in composite technology. Graphene possesses remarkable thermo-mechanical properties and has been reported to be the world's thinnest, strongest and stiffest material (Paulchamy et al. 2015, Phiri et al. 2017). Graphene-reinforced polymer composites are starting to receive industrial interest in energy, composites, sensors, and in the biomedical, automobile and aerospace industries and others. The production of industrial scale graphene composites will require close attention on the effective methods to homogeneously disperse high volumes of graphene filler in high volumes of polymer matrixes for guaranteed interfacial interaction between the two elements. Even though there are some limitations and important factors to consider during the production of graphene

composites, the resultant high performance mechanical property is important for future prospects in composite technology. Thus, graphene-reinforced composites have already begun to gain acceptance among industry practitioners. For example, in the automotive industry, lightweight graphene nanocomposites have been designed as vehicle structural components to enhance both vehicle and occupant safety (Elmarakbi and Azoti 2015). The planned project shows that graphene nanocomposites with multifunctional properties have a promising future demand in both structural and functional composites. Therefore, graphene composite applications are wide ranging and much research is ongoing to build innovative materials for future prospects.

11 Overview and perspectives

The incorporation of graphene into nanocomposites as a filler needs a proper selection and preparation of graphene derivatives. The derivatives of graphene such as graphene, graphite, GO, fGO, and rGO have their own advantages and are possible to be added in a polymer composite. Preparation of those derivatives involved the reduction of GO and the exfoliation of the graphite sheet. The selection of the method depends on final intended graphene form and the designed application of the polymer composite. To date, both graphene and GO can be used as starting materials whether by modifying them or directly using them as fillers in nanocomposites. Graphene is further oxidised and then functionalised to be compatible with polymer matrixes. The key to a force resistance material is the stress transfer between the additive and the parent structure. To create a chemical interaction between the filler and the matrix, both must have similar active sites such as a hydrophilic group to introduce the chemical interaction. To achieve this, graphene is covalently bonded with small molecules or non-covalently bonded to a polymer matrix for potential use in polymer composites. When graphene is ready to form an interaction with a polymer matrix, nanocomposite-processing methods should be considered. The objective in nanocomposite processing methods is to exfoliate the staggered graphene and prepare a homogeneous dispersion of graphene in the polymer matrix. Fully dispersed graphene filler offers more points of interaction in filler-matrix, thus preventing the graphene filler from agglomerating or re-stacking among themselves. More points of interactions reflect more points of stress and heat transfer, thus reinforced mechanical and thermal properties of polymer composite are produced.

12 Conclusion

In summary, extensive properties of graphene have been discovered owing to its unique structure and possible derivatives. In addition, to take advantage of graphene's outstanding properties, an overview of taking graphene as an additive and reinforcing material in manufacturing new and advanced materials were presented. The journey of manipulating graphene started from graphene or GO and ended at various applications such as composites, electrical appliances, electronic parts, thermal barriers, gas barriers and others. Among the variety of applications of graphene in industries, inherited mechanical and thermal properties of graphene into polymer-composite applications are hopefully going to be discovered, as it is useful to produce reinforced mechanical and thermal properties of polymer composites.

A knowledge of the chemistry behind the improved properties of nanocomposites provides valuable insight into graphene reactivity and productivity in the formation of polymer nanocomposites. Much work and research remain to be conducted in developing a variety of sources of polymer matrixes and to study their compatibility with graphene fillers. Besides, there is still more to be accomplished via the exploration of graphene chemistry as the acceptable method for the minimum cost of production of graphene and nanocomposites for industrial scale and industrial use, as reflected by the lack of recent studies in this area. Besides, recently, nanocomposite production has been focussed on synthetic polymers, especially thermoset polymers, and this requires the use of depleted petroleum resources. An aid to this concern would be moving to sustainable natural resources and the transformation from petroleum-based polymers to bio based polymer resources. As a result, the production of graphene reinforced nanocomposites with excellent mechanical performance on an industrial scale, optimum production costs and from renewable resources can be achieved.

Acknowledgement: This work is supported by Research University Grant no. RDU 170361 which the authors gratefully acknowledge.

References

- Abdolmaleki A, Mallakpour S, Karshenas A. Facile synthesis of glucose-functionalized reduced graphene oxide (GFRGO)/poly(vinyl alcohol) nanocomposites for improving thermal and mechanical properties. *Mater Sci Eng B* 2017; 217: 26–35.
- Adak NC, Chhetri S, Kim NH, Murmu NC, Samanta P, Kuila T. Static and dynamic mechanical properties of graphene

- oxide-incorporated woven carbon fiber/epoxy composite. *J Mater Eng Perform* 2018; 27: 1138–1147.
- Alam S, Nizam B, Maksudul U. Synthesis of graphene. *Int Nano Lett* 2016; 6: 65–83.
- Albayrak OO. Bio-Based Polymer Nanocomposites based on layered silicates having a reactive and renewable intercalant. *J Appl Polym Sci* 2013; 130: 2031–2041.
- Alexopoulos N, Paragkiamian Z, Poulin P, Kourkoulis SK. Fracture related mechanical properties of low and high graphene reinforcement of epoxy nanocomposites. *Compos Sci Technol* 2017; 150: 194–204.
- Ali GAM, Makhlof SA, Yusoff MA, Chong KF. Structural and electrochemical characteristics of graphene nanosheets as supercapacitor electrodes. *Rev Adv Mater Sci* 2015; 41: 35–43.
- Al-Shurman KM, Naseem H. CVD graphene growth mechanism on nickel thin film. COMSOL Conference 2014. Boston: USA.
- Amato G. High temperature growth of graphene from cobalt volume: effect on structural properties. *Materials* 2018; 11: 1–14.
- Araby S, Meng Q, Zhang L, Kang H, Majewski P, Tang Y-H, Ma J. Electrically and thermally conductive elastomer/graphene nanocomposites by solution mixing. *Polymers* 2013; 55: 201–210.
- Atif R, Shyha I, Inam F. Mechanical, thermal, and electrical properties of graphene-epoxy nanocomposites – a review. *Polymers* 2016; 8: 281.
- Avouris P, Dimitrakopoulos C. Graphene: synthesis and applications. *Mater Today* 2012; 15: 86–97.
- Awadallah AE, Aboul-Enein AA, Kandil UF, Taha MR. Facile and large-scale synthesis of high quality few-layered graphene nano-platelets via methane decomposition over unsupported iron family catalysts. *Mater Chem Phys* 2017; 191: 75–85.
- Badri MAS, Salleh MM, Noor NFAM, Rahman MYA, Umar AA. Green synthesis of few-layered graphene from aqueous processed graphite exfoliation for graphene thin film preparation. *Mater Chem Phys* 2017; 193: 212–219.
- Baruah P, Karak N. Bio-based tough hyperbranched epoxy/graphene oxide nanocomposite with enhanced biodegradability attribute. *Polym Degrad Stab* 2016; 129: 26–33.
- Berhanuddin NIC, Zaman I, Rozlan SAM, Karim MAA, Manshoor B, Khalid A, Chan SW, Meng Q. Enhancement of mechanical properties of epoxy/graphene nanocomposite Enhancement of mechanical properties of epoxy/graphene nanocomposite. International Conference on Materials Physics and Mechanics, Langkawi, Malaysia, 2017.
- Bora C, Gogoi P, Baglari S, Dolui SK. Preparation of polyester resin/graphene oxide nanocomposite with improved mechanical strength. *J Appl Polym Sci* 2013; 129: 3432–3438.
- Boro U, Karak N. Progress in organic coatings tannic acid based hyperbranched epoxy/reduced graphene oxide nanocomposites as surface coating materials. *Prog Org Coat* 2017; 104: 180–187.
- Byun Y, Coskun A. Bottom-up approach for the synthesis of a three-dimensional nanoporous graphene nanoribbon framework and its gas sorption properties. *Chem Mater* 2015; 27: 2576–2583.
- Cai D, Jin J, Yusoh K, Rafiq R, Song M. High performance polyurethane/functionalized graphene nanocomposites with improved mechanical and thermal properties. *Compos Sci Technol* 2012; 72: 702–707.
- Cao L, Liu X, Na H, Wu Y, Zhenga W, Zhu J. How a bio-based epoxy monomer enhanced the properties of diglycidyl ether of bisphenol A (DGEBA)/graphene composites. *J Mater Chem A* 2013; 1: 5081–5088.
- Chang J, Huang X, Zhou G, Cui S, Hallac PB, Jiang J, Patrick TH, Chen J. Multilayered Si nanoparticle/reduced graphene oxide hybrid as a high-performance lithium-ion battery anode. *Adv Mater* 2014; 26: 758–764.
- Chatterjee S, Chu BTT. Graphene based polymer nanocomposites. In: Aliofkhaezrai M, Ali N, Milne WI, Ozkan CS, Mitura S, Gervasoni JL, editors. *Graphene science handbook: applications and industrialization*. Florida: Taylor and Francis Group, 2016: 145–160.
- Chatterjee S, Wang JW, Kuo WS, Tai NH, Salzmann C, Li WL, Hollertz R, Nüescha FA, Chu BTT. Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites. *Chem Phys Lett* 2012; 531: 6–10.
- Chen J, Yao B, Li C, Shi G. An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon* 2013; 64: 225–229.
- Chhetri S, Chandra N, Samanta P, Chandra N, Kuila T. Functionalized reduced graphene oxide/epoxy composites with enhanced mechanical properties and thermal stability. *Polym Test* 2017; 63: 1–11.
- Chronopoulos DD, Bakandritsos A, Pykal M, Zbořil R, Otyepka M. Chemistry, properties, and applications of fluorographene. *Appl Mater Today* 2017; 9: 60–70.
- Ciesielski A, Samori P. Graphene via sonication assisted liquid-phase exfoliation. *Chem Soc Rev* 2014; 43: 381–398.
- Cui Y, Kundalwal SI, Kumar S. Gas barrier performance of graphene/polymer nanocomposites. *Carbon* 2016; 98: 313–333.
- Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *Chem Soc Rev* 2009; 39: 228–240.
- Ebrahimzadeh S, Ghanbarzadeh B, Hamishehkar H. Physical properties of carboxymethyl cellulose based nano-biocomposites with graphene nano-platelets. *Int J Biol Macromol* 2016; 84: 16–23.
- Eksik O, Maiorana A, Spinella S, Krishnamurthy A, Weiss S, Gross RA, Koratkar N. Nanocomposites of a cashew nut shell derived epoxy resin and graphene platelets: from flexible to tough. *ACS Sustainable Chem Eng* 2016; 4: 1715–1721.
- Elmarakbi A, Azoti WL. Novel composite materials for automotive applications: concepts and challenges for energy-efficient and safe vehicles. 10th International Conference on Composite Science and Technology (ICCST/10), Lisbon, 2015.
- Emiru TF, Ayele DW. Controlled synthesis, characterization and reduction of graphene oxide: a convenient method for large scale production. *Egyptian J Basic App Sci* 2017; 4: 74–79.
- Fang M, Zhang Z, Li J, Zhang H, Lu H, Yang Y. Constructing hierarchically structured interphases for strong and tough epoxy nanocomposites by amine-rich graphene surfaces. *J Mater Chem* 2010; 20: 9635–9643.
- Fang M, Wang K, Lu H, Yang Y, Nutt S. Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites. *J Mater Chem* 2015; 19: 7098–7105.
- Fawaz J, Mittal V. Synthesis of polymer nanocomposites: review of various techniques. In: Mittal V, editor. *Synthesis techniques for polymer nanocomposites*. Germany: Wiley-VCH Verlag GmbH & Co, 2014: 1–30.

- Feng X, Chen W, Yan L. Electrochemical reduction of bulk graphene oxide materials. *RSC Adv* 2016; 6: 80106–80113.
- Ferreira FV, Brito FS, Franceschi W, Simonetti EAN, Cividanes LS, Chipara M, Lozano K. Functionalized graphene oxide as reinforcement in epoxy based nanocomposites. *Surf Interfaces* 2018; 10: 100–109.
- Galpaya D. Synthesis, characterization and applications of graphene oxide-polymer nanocomposites. PhD. Queensland University of Technology, Australian. 2015.
- Galpaya D, Wang M, George G, Motta N, Waclawik E, Yan C. Preparation of graphene oxide/epoxy nanocomposites with significantly improved mechanical properties. *J Appl Phys* 2014; 116: 053518.
- Geim AK, Novoselov KS. The rise of graphene. *Nat Mater* 2007; 6: 183–191.
- Georgakilas V, Tiwari JN, Kemp KC, Perman JA, Bourlinos AB, Kim KS, Zboril R. Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications. *Chem Rev* 2016; 116: 5464–5519.
- Gong LX, Zhao L, Tang LC, Liu HY, Mai YW. Balanced electrical, thermal and mechanical properties of epoxy composites filled with chemically reduced graphene oxide and rubber nanoparticles. *Compos Sci Technol* 2015; 121: 104–114.
- Gong L, Pei Y, Han Q, Zhao L, Wu L, Jiang J, Tang L. Polymer grafted reduced graphene oxide sheets for improving stress transfer in polymer composites. *Comp Sci Tech* 2016; doi: 10.1016/j.compscitech.2016.08.014.
- Guan L, Wan Y, Gong L, Yan D, Tang L, Wu L, Jiang J, Lai G. Toward effective and tunable interphases in graphene oxide/epoxy composites by grafting different chain lengths of polyetheramine onto graphene oxide. *J Mater Chem A* 2014; 2: 15058–15069.
- Guo HL, Wang XF, Qian QY, Wang FB, Xia XH. A green approach to the synthesis of graphene nanosheets. *ACS Nano* 2009; 3: 2653–2659.
- Hameed N, Dumée LF, Alliouf F, Reghat M, Jeffrey S, Naebe M, Magniez K, Parameswaranpillai J, Fox B L. Graphene based room temperature flexible nanocomposites from permanently cross-linked networks. *Sci Rep* 2018; 8: 1–8.
- Haq M, Burgueño R, Mohanty AK, Misra M. Bio-based polymer nanocomposites from UPE/EML blends and nanoclay: development, experimental characterization and limits to synergistic performance. *Compos Part A* 2011; 42: 41–49.
- He S, Petkovich ND, Liu K, Qian Y, Macosko CW, Stein A. Unsaturated polyester resin toughening with very low loadings of GO derivatives. *Polymer* 2017; 110: 149–157.
- Hu K, Kulkarni DD, Choi I, Tsukruk VV. Graphene-polymer nanocomposites for structural and functional applications. *Prog Polym Sci* 2014; 39: 1934–1972.
- Huang X, Qi X, Boey F, Zhang H. Graphene-based composites. *Chem Soc Rev* 2012; 41: 666–686.
- Huang N, Zang J, Zhang G, Guan L, Li S, Zhao L, Tang L. Efficient interfacial interaction for improving mechanical properties of polydimethylsiloxane nanocomposites filled with low content of graphene oxide nanoribbons. *RSC Adv* 2017; 7: 22045–22053.
- Huskić M, Bolka S, Vesel A, Mozeti M, An A, Vizintin A, Ema Ž. One-step surface modification of graphene oxide and influence of its particle size on the properties of graphene oxide/epoxy resin nanocomposites. *Eur Polym J* 2018; 101: 211–217.
- Inagaki M, Kang FY. Graphene derivatives: graphane, fluorographene, graphene oxide, graphyne and graphdiyne. *J Mater Chem A* 2014; 2: 13193–13206.
- Jacobberger RM, Machhi R, Wroblewski J, Taylor B, Gillian-Daniel AL, Arnold MS. Simple graphene synthesis via chemical vapor deposition. *J Chem Educ* 2015; 92: 1903–1907.
- Jang BZ, Zhamu A. Processing of nanographene platelets (NGPs) and NGP nanocomposites: a review. *J Mater Sci* 2008; 43: 5092–5101.
- Jiang L, Niu T, Lu X, Dong H, Chen W, Liu Y, Hu W, Zhu D. Low-temperature, bottom-up synthesis of graphene via a radical-coupling reaction. *J Am Chem Soc* 2013; 135: 9050–9054.
- Jyoti J, Babal AS, Sharma S, Dhakate SR, Singh BP. Significant improvement in static and dynamic mechanical properties of graphene oxide-carbon nanotube acrylonitrile butadiene styrene hybrid composites. *J Mater Sci* 2018; 53: 2520–2536.
- Kang BJ, Mun JH, Hwang CY, Cho BJ. Monolayer graphene growth on sputtered thin film platinum Monolayer graphene growth on sputtered thin film platinum. *J Appl Phys* 2009; doi: 10.1063/1.3254193.
- Kauppila J, Kunnas P, Damlin P, Viinikanoja A, Kvarnström C. Electrochemical reduction of graphene oxide films in aqueous and organic solutions. *Electrochim Acta* 2013; 89: 84–89.
- Kaveh P, Mortezaei M, Barikani M, Khanbabaei G. Low-temperature flexible polyurethane/graphene oxide nanocomposites: effect of polyols and graphene oxide on physicomechanical properties and gas permeability. *Polym Plast Technol Eng* 2014; 53: 278–289.
- Khan ZU, Kausar A, Ullah H. A review on composite papers of graphene oxide, carbon nanotube, polymer/GO, and polymer/CNT: processing strategies, properties, and relevance. *Polym Plast Technol Eng* 2016; 55: 559–581.
- Kim IH, Jeong YG. Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. *J Polym Sci Part B: Polym Phys* 2010; 48: 850–858.
- Kumar PV, Bardhan NM, Chen GY, Li Z, Belcher AM, Grossman JC. New insights into the thermal reduction of graphene oxide: impact of oxygen clustering. *Carbon* 2016; 100: 90–98.
- Kuzhir P, Volynets N, Maksimenko S, Kaplas T, Svirko Y. Multilayered graphene in Ka-band: nanoscale coating for aerospace applications. *J Nanosci Nanotechnol* 2013; 13: 5864–5867.
- Le MT, Huang SC. Thermal and mechanical behaviour of hybrid polymer nanocomposite reinforced with graphene nanoplatelets. *Materials* 2015; 8: 5526–5536.
- Lee CH, Tseng WH, Yang CK. Electronic structures of hybrid graphane/boron nitride nanoribbons with hydrogen vacancies. *AIP Adv* 2017; 7: 75118.
- Li Y, Pan D, Chen S, Wang Q, Pan G, Wang T. In situ polymerization and mechanical, thermal properties of polyurethane/graphene oxide/epoxy nanocomposites. *Mater Des* 2013; 47: 850–856.
- Li W, Li H, Yang X, Feng W. Preparation and properties of novel sulfonic graphene oxide – epoxy resin nanocomposites by resin transfer molding process. *J Compos Mater* 2016; 51: 1097–1208.
- Li Y, Zhang H, Porwal H, Huang Z, Bilotti E, Peijs T. Mechanical, electrical and thermal properties of in-situ exfoliated graphene/epoxy nanocomposites. *Compos Part A* 2017; 95: 229–236.
- Lin J, Zhang P, Zheng C, Wu X, Mao T, Zhu M, Wang H, Feng D, Qian S, Cai X. Reduced silanized graphene oxide/epoxy-polyurethane composites with enhanced thermal and mechanical properties. *Appl Surf Sci* 2014; 316: 114–123.

- Liu J. Electrochemical exfoliation synthesis of graphene. In *Graphene-based composites for electrochemical energy storage*. Singapore: Springer, 2017: 39–50.
- Liu H, Li Y, Wang T, Wang Q. In situ synthesis and thermal, tribological properties of thermosetting polyimide/graphene oxide nanocomposites. *J Mater Sci* 2012; 47: 1867–1874.
- Liu T, Zhao Z, Tjiu WW, Lv J, Wei C. Preparation and characterization of epoxy nanocomposites containing surface-modified graphene oxide. *J Appl Polym Sci* 2014; 131: 1–6.
- Ljubic D, Srinivasan M, Szoszkiewicz R, Javni I, Petrović ZS. Surface modified graphene/single-phase polyurethane elastomers with improved thermo-mechanical and dielectric properties. *Eur Polym J* 2015; 70: 55–65.
- Loh KP, Bao Q, Ang PK, Yang J. The chemistry of graphene. *J Mater Chem* 2010; 20: 2277–2289.
- Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM. Improved synthesis of graphene oxide. *ACS Nano* 2010; 4: 4806–4814.
- Mauro M, Acocella MR, Corcione CE, Maffezzoli A, Guerra G. Catalytic activity of graphite-based nanofillers on cure reaction of epoxy resins. *Polymer* 2014; 55: 5612–5615.
- Mustapha SNH, Rahmat AR, Arsad A. Bio-based thermoset nanocomposite derived from vegetable oil: a short review. *Rev Chem Eng* 2014; 30: 167–182.
- Naebe M, Wang J, Amini A, Khayyam H, Hameed N, Li LH, Chen Y, Fox B. Mechanical property and structure of covalent functionalised graphene/epoxy nanocomposites. *Sci Rep* 2014; 4: 4375.
- Nam J, Kim DC, Yun H, Shin DH, Nam S, Lee WK, Weman H, Kim KS. Chemical vapor deposition of graphene on platinum: growth and substrate interaction. *Carbon* 2017; 111: 733–740.
- Narimissa E, Gupta RK, Kao N, Choi HJ, Jollands M, Bhattacharya SN. Melt rheological investigation of polylactide-nanographite platelets biopolymer composites. *Polym Eng Sci* 2014; 54: 175–188.
- Nguyen DA, Lee YR, Raghu AV, Jeong HM, Shin CM, Kim BK. Morphological and physical properties of a thermoplastic polyurethane reinforced with functionalized graphene sheet. *Polym Int* 2009; 58: 412–417.
- Pal N, Dubey P, Gopinath P, Pal K. Combined effect of cellulose nanocrystal and reduced graphene oxide into poly-lactic acid matrix nanocomposite as a scaffold and its anti-bacterial activity. *Int J Biol Macromol* 2017; 95: 94–105.
- Papageorgiou DG, Kinloch IA, Young RJ. Graphene/elastomer nanocomposites. *Carbon* 2015; 95: 460–484.
- Park OK, Kim SG, You NH, Ku BC, Hui D, Lee JH. Synthesis and properties of iodo functionalized graphene oxide/polyimide nanocomposites. *Compos Part B* 2014; 56: 365–371.
- Park YT, Qian Y, Chan C, Suh T, Nejhad MG, Macosko CW, Stein A. Epoxy toughening with low graphene loading. *Adv Funct Mater* 2015; 25: 575–585.
- Parvez K, Wu ZS, Li R, Liu X, Graf R, Feng X, Müllen K. Exfoliation of graphite into graphene in aqueous solutions of inorganic salts. *J Am Chem Soc* 2014; 136: 6083–6091.
- Pathak AK, Borah M, Gupta A, Yokozeki T, Dhakate SI. Improved mechanical properties of carbon fiber/graphene oxide-epoxy hybrid composites. *Compos Sci Technol* 2016; 135: 28–38.
- Paulchamy B, Arthi G, Lignesh BD. A simple approach to stepwise synthesis of graphene oxide nanomaterial. *J Nanomed Nanotechnol* 2015; 6: 1–4.
- Pei S, Cheng HM. The reduction of graphene oxide. *Carbon* 2012; 50: 3210–3228.
- Peng Q, Dearden AK, Crean J, Han L, Liu S, Wen X, De S. New materials graphyne, graphdiyne, graphone, and graphane: review of properties, synthesis, and application in nanotechnology. *Nanotechnol Sci Appl* 2014; 7: 1–29.
- Phiri J, Gane P, Maloney TC. General overview of graphene: production, properties and application in polymer composites. *Mater Sci Eng B* 2017; 215: 9–28.
- Pinto AM, Gonçalves C, Gonçalves IC, Magalhães FD. Effect of biodegradation on thermo-mechanical properties and biocompatibility of poly (lactic acid)/graphene nanoplatelets composites. *Eur Polym J* 2016; 85: 431–444.
- Pop E, Varshney V, Roy AK. Thermal properties of graphene: fundamentals and applications. *MRS Bulletin* 2012; 37: 1273–1281.
- Potts JR, Dreyer DR, Bielawski CW, Ruoff RS. Graphene-based polymer nanocomposites. *Polymer* 2011; 52: 5–25.
- Pour ZS, Ghaemy M. Polymer grafted graphene oxide: for improved dispersion in epoxy resin and enhancement of mechanical properties of nanocomposite. *Compos Sci Technol* 2016; 136: 145–157.
- Prolongo SG, Jimenez-Suarez A, Moriche R, Ureña A. In situ processing of epoxy composites reinforced with graphene nanoplatelets. *Compos Sci Technol* 2013; 86: 185–191.
- Qiu J, Wang S. Enhancing polymer performance through graphene sheets. *J Appl Polym Sci* 2011; 119: 3670–3674.
- Qiu Y, Wang J, Wu D, Wang Z, Zhang M, Yao Y, Wei N. Thermoplastic polyester elastomer nanocomposites filled with graphene: mechanical and viscoelastic properties. *Compos Sci Technol* 2016; 132: 108–115.
- Rafiee MA, Rafiee J, Wang Z, Song H, Yu ZZ, Koratkar N. Enhanced mechanical properties of nanocomposites at low graphene content. *ACS Nano* 2009; 3: 3884–3890.
- Ramezanzadeh B, Ghasemi E, Mahdavian M, Changizi E, Moghadam MM. Characterization of covalently-grafted polyisocyanate chains onto graphene oxide for polyurethane composites with improved mechanical properties. *Chem Eng J* 2015; 281: 869–883.
- Ren PG, Liu XH, Ren F, Zhong GJ, Ji X, Xu L. Biodegradable graphene oxide nanosheets/poly-(butylene adipate-co-terephthalate) nanocomposite film with enhanced gas and water vapor barrier properties. *Polym Test* 2017; 58: 173–180.
- Renteria JD, Nika DL, Balandin AA. Graphene thermal properties: applications in thermal management and energy storage. *Appl Sci* 2014; 4: 525–547.
- Rohini R, Katti P, Bose S. Tailoring the interface in graphene/thermoset polymer composites: a critical review. *Polymer* 2015; 70: A17–A34.
- Rozhkov AV, Sboychakov AO, Rakhmanov AL, Nori F. Electronic properties of graphene-based bilayer systems. *Physics Rep* 2016; 648: 1–132.
- Rus AZM, Abdullah NM, Abdullah MFL, Idris M. Graphite/bio-based epoxy composites: the mechanical properties interface. *Applied Mechanics and Materials*. Stafa-Zurich, Switzerland 2015; 799: 153–157.
- Sahin H, Leenaerts O, Singh SK, Peeters FM. Graphane: from synthesis to applications. *Wiley Interdiscip Rev Comput Mol Sci* 2015; 5: 255–272.
- Sainsbury T, Gnanih S, Spencer SJ, Mignuzzi S, Belsey NA, Paton KR, Satti A. Extreme mechanical reinforcement in

- graphene oxide based thin-film nanocomposites via covalently tailored nanofiller matrix compatibilization. *Carbon* 2017; 114: 367–376.
- Salavagione HJ, Martinez G, Ellis G. Graphene-based polymer nanocomposites. In: Mikhailov S, editor. *Physics and applications of graphene – experiments*. Croatia: Intech, 2011: 169–192.
- Saleem H, Edathil A, Ncube T, Pokhrel J, Khoori S, Abraham A, Mittal V. Mechanical and thermal properties of thermoset – graphene nanocomposites. *Macromol Mater Eng* 2016; 301: 231–259.
- Satti A, Larpent P, Gun'ko Y. Improvement of mechanical properties of graphene oxide/poly (allylamine) composites by chemical crosslinking. *Carbon* 2010; 48: 3376–3381.
- Scaffaro R, Botta L, Maio A, Gallo G. PLA graphene nanoplatelets nanocomposites: physical properties and release kinetics of an antimicrobial agent. *Composites Part B* 2017; 109: 138–146.
- Seung HH. Thermal reduction of graphene oxide. In: Mikhailov S, editor. *Physics and applications of graphene – experiments*. Croatia: InTech, 2011: 73–90.
- Shah R, Kausar A, Muhammad B, Shah S. Progression from graphene and graphene oxide to high performance polymer-based nanocomposite: a review. *Polym Plast Technol Eng* 2015; 54: 173–183.
- Shang LL, Westwood AVK, Drummond-Brydson R. Graphene synthesis via electrochemical exfoliation of graphite nanoplatelets in aqueous sulphuric acid. In: *Carbon 2016, 10–15 Jul 2016, Pennsylvania, USA: Pennsylvania State University*. (Unpublished)
- Shen J, Shi M, Ma H, Yan B, Li N, Hu Y, Ye M. Synthesis of hydrophilic and organophilic chemically modified graphene oxide sheets. *J Colloid Interface Sci* 2010; 352: 366–370.
- Shen J, Yan B, Shi M, Ma H, Li N, Ye M. Synthesis of graphene oxide-based biocomposites through diimide-activated amidation. *J. Colloid Interface Sci.* 2011; 356: 543–549.
- Singh V, Joung D, Zhai L, Das S, Khondaker SI, Seal S. Graphene based materials: past, present and future. *Prog Mater Sci* 2011; 56: 1178–1271.
- Sisti L, Belcari J, Mazzocchetti L, Totaro G, Vannini M, Giorgini L, Zucchelli A, Celli A. Multicomponent reinforcing system for poly(butylene succinate): composites containing poly(l-lactide) electrospun mats loaded with graphene. *Polym Test* 2016; 50: 283–291.
- Song SH, Park KH, Kim BH, Choi YW, Jun GH, Lee DJ, Kong BS, Paik KW, Jeon S. Enhanced thermal conductivity of epoxy – graphene composites by using non-oxidized graphene flakes with non-covalent functionalization. *Adv Mater* 2013; 25: 732–737.
- Sridhar V, Lee I, Chun HH, Park H. Graphene reinforced biodegradable poly (3-hydroxybutyrate-co-4-hydroxybutyrate) nano-composites. *Express Polymer Letters* 2013; 7: 320–328.
- Sun Y, Tang B, Huang W, Wang S, Wang Z, Wang X, Zhu Y, Tao C. Preparation of graphene modified epoxy resin with high thermal conductivity by optimizing the morphology of filler. *Appl Therm Eng* 2016; 103: 892–900.
- Surudžić R, Janković A, Bibić N, Vukašinović-Sekulić M, Perić-Grujić A, Mišković-Stanković V, Park SJ, Rhee KY. Physico-chemical and mechanical properties and antibacterial activity of silver/poly (vinyl alcohol)/graphene nanocomposites obtained by electrochemical method. *Composites Part B* 2016; 85: 102–112.
- Svendsen EM. Graphene Oxide as Reinforcement in Epoxy Based Nanocomposites. Master's, Norwegian University of Science and Technology, Norway, 2014.
- Tang L, Li X, Ji R, Teng KS, Tai G, Ye J, Wei C, Lau SP. Bottom-up synthesis of large-scale graphene oxide nanosheets. *J Mater Chem* 2012a; 22: 5676–5683.
- Tang Z, Kang H, Shen Z, Guo B, Zhang L, Jia D. Grafting of polyester onto graphene for electrically and thermally conductive composites. *Macromolecules* 2012b; 45: 3444–3451.
- Tang LC, Wan YJ, Yan D, Pei YB, Zhao L, Li YB, Wu LB, Jiang JX, Lai GQ. The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* 2013; 60: 16–27.
- Tang B, Hu G, Gao H, Hai L. Application of graphene as filler to improve thermal transport property of epoxy resin for thermal interface materials. *Int J Heat Mass Transfer* 2015; 85: 420–429.
- Tang XZ, Mu C, Zhu W, Yan X, Hu X, Yang J. Flexible polyurethane composites prepared by incorporation of polyethylenimine-modified slightly reduced graphene oxide. *Carbon* 2016a; 98: 432–440.
- Tang X, Zhou Y, Peng M. Green preparation of epoxy/graphene oxide nanocomposites using a glycidylamine epoxy resin as the surface modifier and phase transfer agent of graphene oxide. *ACS Appl Mater Interfaces* 2016b; 8: 1854–1866.
- Tegou E, Pseiropoulos G, Filippidou MK, Chatzandroulis S. Low-temperature thermal reduction of graphene oxide films in ambient atmosphere: infra-red spectroscopic studies and gas sensing applications. *Microelectron Eng* 2016; 159: 146–150.
- Toh SY, Loh KS, Kamarudin SK, Daud WRW. Graphene production via electrochemical reduction of graphene oxide: synthesis and characterisation. *Chem Eng J* 2014; 251: 422–434.
- Tour JM. Top-down versus bottom-up fabrication of graphene-based electronics. *Chem Mater* 2013; 26: 163–171.
- Verdejo R, Bernal MM, Romasanta LJ, Lopez-Manchado MA. Graphene filled polymer nanocomposites. *J Mater Chem* 2011; 21: 3301–3310.
- Wan C, Chen B. Poly (ϵ -caprolactone)/graphene oxide biocomposites: mechanical properties and bioactivity. *Biomed Mater* 2011; 6: 055010–055018.
- Wan Y, Tang L, Gong L, Yan D, Li Y. Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties. *Carbon* 2013; 69: 467–480.
- Wan Y, Gong L, Tang L, Wu L, Jiang J. Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. *Compos Part A* 2014; doi:http://doi.org/10.1016/j.compositesa.2014.04.023.
- Wang X, Jin J, Song M. An investigation of the mechanism of graphene toughening epoxy. *Carbon* 2013; 65: 324–333.
- Wang M, Wang C, Song Y, Xie H, Huang Y. One-pot in situ polymerization of graphene oxide nanosheets and poly (p-phenylenebenzobisoxazole) with enhanced mechanical and thermal properties. *Compos Sci Technol* 2017; 141: 16–23.
- Woh LW. Development of reduced graphene oxide/high density polyethylene (RGO/HDPE) high performance nanocomposites. PhD. Universiti Tuanku Abdul Rahman, Malaysian, 2015.
- Wong CPP, Lai CW, Lee KM, Hamid SBA. Advanced chemical reduction of reduced graphene oxide and its photocatalytic activity in degrading reactive black 5. *Materials* 2015; 8: 7118–7128.

- Xing W, Yuan B, Wang X, Hu Y. Enhanced mechanical properties, water stability and repeatable shape recovery behavior of Ca²⁺ crosslinking graphene oxide-based nacre-mimicking hybrid film. *Mater Des* 2017; 115: 46–51.
- Xu H, Gong L, Wang X, Zhao L, Pei Y, Wang G, Liu Y, Wu L, Jiang J, Tang L. Influence of processing conditions on dispersion, electrical and mechanical properties of graphene-filled-silicone rubber composites. *Compos Part A* 2016; 91: 53–64.
- Yadav SK, Cho JW. Functionalized graphene nanoplatelets for enhanced mechanical and thermal properties of polyurethane nanocomposites. *Appl Surf Sci* 2013; 266: 360–367.
- Yang X, Li L, Shang S, Tao XM. Synthesis and characterization of layer-aligned poly (vinyl alcohol)/graphene nanocomposites. *Polymer* 2010; 51: 3431–3435.
- Yang X, Shang S, Li L. Layer-structured poly (vinyl alcohol)/graphene oxide nanocomposites with improved thermal and mechanical properties. *J Appl Polym Sci* 2011; 120: 1355–1360.
- Yao X, Gao X, Jiang J, Xu C, Deng C, Wang J. Comparison of carbon nanotubes and graphene oxide coated carbon fiber for improving the interfacial properties of carbon fiber/epoxy composites. *Compos part B* 2018; 132: 170–177.
- Ye S, Feng J. Self-assembled three-dimensional hierarchical graphene/polypyrrole nanotube hybrid aerogel and its application for supercapacitors. *ACS Appl Mater Interfaces* 2014; 6: 9671–9679.
- Young RJ, Kinloch IA, Gong L, Novoselov KS. The mechanics of graphene nanocomposites: a review. *Compos Sci Technol* 2012; 72: 1459–1476.
- Yuan XY, Zou LL, Liao CC, Dai JW. Improved properties of chemically modified graphene/poly (methyl methacrylate) nanocomposites via a facile in-situ bulk polymerization. *Express Polym Lett* 2012; 6: 847–858.
- Zaid RM, Chin F, Yi E, Teo L, Ng E, Feng KC. Reduction of graphene oxide nanosheets by natural beta carotene and its potential use as supercapacitor electrode. *Arabian J Chem* 2015; 8: 560–569.
- Zang J, Wan Y, Zhao L, Tang L. Fracture behaviors of TRGO-filled epoxy nanocomposites with different dispersion/interface levels. *Macromol Mater Eng* 2015; 300: 737–749.
- Zhang HB, Zheng WG, Yan Q, Yang Y, Wang JW, Lu ZH, Ji GY, Yu ZZ. Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding. *Polymer* 2010; 51: 1191–1196.
- Zhang X, Zhang DC, Chen Y, Sun XZ, Wang CG, Ma YW. Electrochemical reduction of graphene oxide films: preparation, characterization and their electrochemical properties. *Chin Sci Bull* 2012; 57: 3045–3050.
- Zhang L, Jiao H, Jiu H, Chang J, Zhang S, Zhao Y. Thermal, mechanical and electrical properties of polyurethane/(3-aminopropyl) triethoxysilane functionalized graphene/epoxy resin interpenetrating shape memory polymer composites. *Composites Part A* 2016; 90: 286–295.
- Zheng W, Wong SC. Electrical conductivity and dielectric properties of PMMA/expanded graphite composites. *Compos Sci Technol* 2003; 63: 225–235.
- Zheng R, Xu Z, Khanaki A, Tian H, Zuo Z, Zheng JG, Liu J. Low temperature growth of graphene on iron substrate by molecular beam epitaxy. *Thin Solid Films* 2017; 627: 39–43.

Bionotes



Nur Bazilah Thalib

Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Nur Bazilah Thalib is a MSc candidate in Advanced Material at University Malaysia Pahang, Malaysia. She received her BSc from the University of Leeds, UK. She is currently studying sustainable composite related to graphene reinforced bio-based thermoset composites for her Master's study.

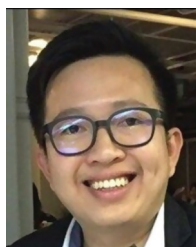
Siti Noor Hidayah Mustapha

Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia, snhidayah@ump.edu.my.

<https://orcid.org/0000-0002-4107-6074>



Siti Noor Hidayah Mustapha is a senior lecturer at the Universiti Malaysia Pahang, Malaysia. She obtained her undergraduate degree in Engineering (Chemical-Polymer) in 2011 and her PhD in Polymer Engineering from Universiti Teknologi Malaysia in 2016. Her PhD was on composite material from renewable sources (supervisor: Assoc. Prof. Dr Abdul Razak Rahmat). She has published several research papers and conference proceedings on bioplastic, biopolymer and biocomposite materials. Currently, her research is focussed on bioresin development and reinforcement for composite applications.



Chong Kwok Feng

Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Chong Kwok Feng received his BSc degree in 2004 from the Universiti Teknologi Malaysia, followed by a PhD in 2010 from the National University of Singapore. His PhD work focussed on the development of carbon nanomaterials for biosensing applications, supervised by Prof. Kian Ping Loh. In 2010, he went to Universiti Malaysia Pahang (UMP) as a lecturer in Chemistry and was promoted to an Associate Professorship in 2016. He established a carbon research group in UMP to work on the application of carbon materials for energy storage and biosensors.

**Rohani Mustapha**

School of Ocean Engineering, Universiti
Malaysia Terengganu, 21030, Kuala
Terengganu, Terengganu, Malaysia

Rohani Mustapha is part of the young academic training scheme staff at the School of Ocean Engineering, Universiti Malaysia Terengganu. She has published several research papers and conference proceedings on natural fibres and composites. She is currently pursuing studies at Universiti Teknologi Malaysia and conducts research on bio-based epoxy nanocomposites with bio-based hardeners.