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Synthesis, Characterization and Applications of
Graphene Oxide-Polymer Nanocomposites

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Abstract

Graphene consists of a single layer of sp^2 hybridized carbon atoms forming a two-dimensional (2D) hexagonal lattice. A unique combination of excellent electrical, thermal and mechanical properties has made graphene a material for multi-functional reinforcement for polymers. Graphene incorporated-polymer nanocomposites show greater mechanical, thermal, and electrical properties compared to neat polymer which can find applications in the field of automotive, aerospace, electronics and green energy. The overall performance of filler reinforced polymer composites depends not only on the properties of the individual components but also on the interactions between the filler and the polymer matrix at the contact surfaces. The physical, mechanical and even chemical composition of this interphase region is different from the bulk polymer matrix. Experimental as well as theoretical approaches can be employed to evaluate the micromechanical properties and the chemistry of interphase. Studies have been conducted to evaluate the interphase properties of fibre-polymer, CNT-polymer composites. However, few studies have investigated graphene-polymer interphase. Due to lack of understanding of the chemical nature and material behaviour at the interface, toughening and strengthening mechanisms in graphene-polymer nanocomposites are not well understood. Therefore, the main theme of this thesis was to evaluate the microstructure and the properties of graphene-polymer interphase, thereby achieving a fundamental understanding of the reinforcing behaviour of graphene in polymer nanocomposites.

In order to achieve optimal enhancement in the property of graphene-polymer nanocomposites, the homogeneous dispersion of graphene into the matrix, and the strong interfacial interactions between the graphene and the matrix are required. This can be achieved by use of graphene oxide (GO) as graphene nanofiller due to its oxygen containing functional groups which can make it more compatible and uniformly dispersed in polymer matrices due to stronger interactions with the polymer matrix compared to pristine graphene. In the paper 1 presented in chapter 3, the effects of GO on the mechanical and thermal properties of epoxy resin were investigated. Epoxy resin was chosen because the polymer matrix has high stiffness, dimensional stability and chemical resistance which make it the most important thermosetting resin in industry as structural and functional composites for

applications in automobile, aerospace and electronics. It is demonstrated that the GO-epoxy nanocomposites fabricated in this work have shown excellent mechanical properties. At loading of ~ 0.1 wt% GO was found to increase the mode I fracture toughness (K_{Ic}) of the neat epoxy by nearly 50%. The Young's modulus of 0.1 wt% GO-epoxy was $\sim 28\%$ larger than neat epoxy and the maximum enhancement of $\sim 36\%$ was achieved at 0.5 wt% GO loading. There was slight improvement in ultimate tensile strength with GO incorporation and 0.1 wt% GO-epoxy showed $\sim 7\%$ increase compared to the control i.e. neat epoxy matrix. Differential scanning calorimetry results showed that GO addition moderately affects the glass transition temperature (T_g) of epoxy. The maximum decrease of T_g by $\sim 7^\circ\text{C}$ was shown for the nanocomposite with 0.5 wt% GO. Fractography analysis of the tested samples revealed that the toughening mechanism of GO nanocomposite is crack deflection.

As it was found that GO can effectively improve the fracture toughness of epoxy matrix, in paper 2 presented in chapter 4, the chemistry and reaction mechanisms at the GO-epoxy interphase were evaluated in order to understand the toughening improvement by GO from a chemistry perspective. However, it was recently found that the micromechanical environment of GO appears to be much more complex than the oversimplification commonly used to describe the enhanced fracture toughness of epoxy nanocomposites due to the presence of highly oxidized low molecular weight organic fragments called oxidative debris (OD). OD greatly impacts the GO-resin interfacial chemistry. Therefore, in this kinetic study, a new approach is discovered to evaluate the influence of as-produced GO (aGO) and OD free, autoclaved GO (acGO) on cure and fracture toughness of epoxy by Fourier Transform Infrared Emission Spectroscopy (FT-IES) and Differential Scanning Calorimetry (DSC). Results demonstrate that the presence of OD on the GO greatly influences the cure kinetics, mainly lowering the crosslinking capacity of aGO-resin interphase. Moreover, OD itself catalyses the epoxide ring opening reaction and promotes homopolymerization which would also produce lower crosslinking density. The difference in cross-link densities was reflected in DSC data that showed aGO nanocomposite exhibited lower T_g and acGO nanocomposite exhibited higher T_g compared to neat resin. Therefore, our findings demonstrate that these chemical changes in the interphase compared to bulk are consistent with the result that low addition of aGO (commonly used as GO in polymer nanocomposites) can effectively improve the toughness of epoxy matrix.

Further, in this thesis, new approaches to making capacitors and gas sensors based on GO were attempted which promise a simple and easy avenue for developing such devices at a larger scale. Paper 3 in chapter 5 reports a new approach to harness these properties in fabricating supercapacitors. Thin film capacitors were fabricated by using graphene and GO as charge storage and dielectric spacer, respectively. Results show that fabricated devices exhibited high capacitance due to a high dielectric constant and electrical resistivity. It also suggested that graphene could be a good electrode material for supercapacitors.

It has been shown that graphene can be used as sensing material to detect various gas molecules. The graphene-based gas sensors detect conductivity change upon adsorption of gas molecules which could arise from the changes of charge carrier concentration in the graphene induced by adsorbed gas molecules. Sensitivity and selectivity of graphene could be engineered by introducing dopants or defects. Paper 4 in chapter 6 reveals that doping of GO with Cs_2CO_3 (GO-Cs) can significantly enhanced the sensitivity of graphene for NO_2 gas at room temperature. The GO-Cs sensor exhibited a significant response to NO_2 , down to concentrations as low as ~ 91 ppb, while GO sensor did not show any response to concentrations below 3ppm. The GO-Cs sensor exhibits a good repeatability compared to GO sensors. Both sensors show a reduction of resistivity upon exposure to the gas which could be attributed to a negative charge transferred to NO_2 molecules resulting in p-type behaviour. The sensitivity enhancement in GO-Cs could be attributed to defects introduced into the GO-Cs films during the doping process.

The findings presented in this thesis have provided not only fundamental understanding of chemical and mechanical behaviour at the interphase of GO-resin nanocomposites but also applications of GO in other potential fields.

Publications List

Journal Articles

1. D. Galpaya; M. Wang; G. George; N. Motta; E. Waclawik; C. Yan, *Preparation of Graphene Oxide/Epoxy Nanocomposites with Significantly Improved Mechanical Properties*, Journal of Applied Physics, **2014**, 116, 053518, [doi:10.1063/1.4892089](https://doi.org/10.1063/1.4892089)
2. D. Galpaya; M. Wang; C. Yan; M. Liu; N. Motta; E. Waclawik, *Fabrication and Mechanical and Thermal Behaviour of Graphene Oxide/Epoxy Nanocomposites*, Journal of Multifunctional Composites, **2013**, 91-98, [doi:10.12783/issn.2168-4286/1.2/Galpaya](https://doi.org/10.12783/issn.2168-4286/1.2/Galpaya)
3. D. Galpaya; M. Wang; M. Liu; N. Motta; E. Waclawik; C. Yan, *Recent Advances in Fabrication and Characterization of Graphene-Polymer Nanocomposites*, Graphene, **2012**, 1, 30-49, [doi:10.4236/graphene.2012.12005](https://doi.org/10.4236/graphene.2012.12005)
4. D. Galpaya; J. Fernando; L. Rintoul; N. Motta; E. Waclawik; C. Yan; G. George, *The Effect of Graphene Oxide and its Oxidized Debris on the Cure Chemistry and Interphase Structure of Epoxy Nanocomposites*, Polymer, **2015**, Accepted with minor corrections.
5. C. Piloto; M. Notarianni; M. Shafiei; E. Taran; D. Galpaya; C. Yan; N. Motta, *Highly NO₂ Sensitive Caesium Doped Graphene Oxide Conductometric Sensors*, Beilstein Journal of Nanotechnology, **2014**, 5, 1073-1081, [doi: 10.3762/bjnano.5.120](https://doi.org/10.3762/bjnano.5.120)
6. J. Liu; D. Galpaya; M. Notarianni; C. Yan; N. Motta, *Graphene-based Thin Film Supercapacitor with Graphene Oxide as Dielectric Spacer*, Applied Physics Letters, **2013**, 103, 063108, [doi: 10.1063/1.4818337](https://doi.org/10.1063/1.4818337)
7. M. Wang; Z. Lai; D. Galpaya; C. Yan; N. Hu; L. Zhou, *Atomistic Simulation of Surface Functionalization on the Interfacial Properties of Graphene-Polymer Nanocomposites*, Journal of Applied Physics, **2014**, 115, 123520. doi.org/10.1063/1.4870170

8. M. Wang; D. Galpaya; Z. Lai; Y. Xu; C. Yan, *Surface Functionalization on the Thermal Conductivity of Graphene-Polymer Nanocomposites*, International Journal of Smart and Nano Materials, **2014**, 5, 123-132, doi.org/10.1080/19475411.2014.904828
9. M. Wang; C. Yan; D. Galpaya; Z.B. Lai; L. Ma; N. Hu, Q. Yuan; R. Bai; L. Zhou, *Molecular Dynamics Simulation of Fracture Strength and Morphology of Defective Graphene*. Journal of Nano Research, **2013**, 23, 43-49, 10.4028/www.scientific.net/JNanoR.23.43
10. M. Njuguna; D. Galpaya; C. Yan; J. Colwell; G. Will; N. Hu; P. Yarlagadda; J. Bell, *Investigation on Temperature-Dependent Electrical Conductivity of Carbon Nanotube/Epoxy Composites for Sustainable Energy Applications*, Journal of nanoscience and nanotechnology, **2015**, 15, 1-8, [doi:10.1166/jnn.2015.10514](https://doi.org/10.1166/jnn.2015.10514)

Conference papers

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17. M. Liu; D. Galpaya; C. Yan; J. Bell, *Facile Preparation of Zinc oxide/Reduced Graphene Oxide Composite for Degradation of Rhodamine B*, Oral presentation, 1st International conference on Emerging Advanced Nanomaterials 2012 (ICEAN 2012), 22-25 October **2012**, Brisbane.

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List of Abbreviations

2D	Two Dimensional
CNT	Carbon Nanotubes
CVD	Chemical Vapour Deposition
DDM	4,4'-diaminodiphenylmethane
DGEBA	Diglycidyl ether of bisphenol A
EG	Expanded Graphite
FT-IES	Fourier Transform Infrared Emission Spectroscopy
GICs	Graphite Intercalated Compounds
GNRs	Graphene Nanoribbons
GO	Graphene Oxide
HOPG	Highly-Ordered Pyrolytic Graphite
OD	Oxidative Debris
QHE	Quantum Hall Effect
T _g	Glass Transition Temperature

Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

QUT Verified Signature

Signature:

Date: 16/06/2015

1 Introduction

1.1 Background

Graphene, an atomic layer of sp^2 hybridized carbon atoms arranged in a hexagonal structure, has shown many unique properties, such as high Young's modulus (~ 1 TPa), the quantum hall effect (QHE), high carrier mobility at room temperature ($\sim 10\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), large specific surface area ($2630\text{ m}^2\text{ g}^{-1}$), good optical transparency ($\sim 97.7\%$), and excellent thermal conductivity ($3000\text{--}5000\text{ W m}^{-1}\text{ K}^{-1}$).¹⁻² Today, graphene has attracted much attention of scientific community; because it shows good potential for use in many emerging areas including polymer composites.

Polymer nanocomposites based on graphene and its derivatives have been developed, based on a range of polymers including epoxy, poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), Polyethylene (PE).³⁻⁷ The superior properties of graphene are reflected in graphene-incorporated polymer nanocomposites, showing greater mechanical, thermal, and electrical properties compared to the neat polymer. This opens a new avenue for developing high strength, light-weight structural polymer composites and applications in the field of automotive, aerospace, electronics and green energy.^{1, 8-9} However, to best exploit the fascinating properties of graphene for composite applications, it is necessary to incorporate and homogeneously disperse them in various polymers. Graphene sheets usually tend to form aggregates in solvents and polymer matrices due to strong graphene-graphene intermolecular van der Waals interactions and high specific surface area, consequently this limits dispersion and exfoliation.¹⁰ Such agglomerations lower the effectiveness of graphene for reinforcement, as maximal load transfer and lowest filling load can only be achieved when the graphene is dispersed at the molecular level in the polymer matrix.¹¹ The atomically smooth surface of pristine graphene has also been shown to have low interfacial strength compared to wrinkled surface of other forms of graphene which is often reported as a favourable medium for creating a robust interface able to locally interlock with the matrix.⁵ In contrast, graphene oxide (GO) possesses abundant oxygen-containing polar functionalities such as carbonyl, hydroxyl, and epoxides groups which can be choices for functionalization and better interactions with various polymers.¹² A

number of GO-polymer nanocomposites have been developed^{5, 13-15}, however, it is still not clear that how the surface chemistry of GO sheets influences the physical properties of polymer nanocomposites.

A feature of polymer-graphene nanocomposites is that very low loadings are required to achieve significant changes in the properties which imply that the structure of interphase should mainly be responsible for property enhancements. Investigation on polymer-graphene interphase is limited and so its effects on the overall composite are to a large extent, still unknown. Due to the lack of information on material behaviour at the interface, toughening and strengthening mechanisms in graphene-polymer nanocomposites are not well understood. More research is required to gain complete understanding of the micro-structure and micro-properties of the interphase and so to understand the reinforcing as well as failure mechanisms at the interface.

This study focused on investigating the interfacial behaviour between graphene fillers and polymer at the nanoscale. In this project, epoxy was selected to fabricate graphene oxide nanocomposites. Epoxy is a most important thermosetting resin in industry, as structural and functional composites for applications in automobile, aerospace and electronics because of its high stiffness, dimensional stability and chemical resistance. The first part of this research conducted included on evaluation of mechanical performance of graphene oxide-epoxy nanocomposites, with variation of weight fraction of GO. Property enhancement and toughening mechanisms of nanocomposites was found to be well-correlated with nanocomposite micro-structure. Since, the property improvement in epoxy nanocomposites highly depends on the formation of the cross-linked molecular network structure in the system, several research groups have worked on understanding the influence of graphene fillers on cure and the reaction mechanisms of epoxy nanocomposites but there has been inconsistency in reported results.^{5, 16-17} This suggests that further studies are needed for rationalization of these contradictory findings. In the current study, combined infrared emission spectroscopy (IES) and differential scanning calorimetry (DSC) provided in-depth information about the cure kinetics and chemical bond formation between GO and epoxy polymer matrix during the cure process and consequently chemical structure of the GO-epoxy interphase.

It has been recently reported that as-produced GO consists of highly oxidized low molecular weight polyaromatic fragments called oxidative debris (OD).¹⁸ This

OD is a by-product of the oxidation process and can be strongly absorbed to the GO surfaces. OD can be isolated by washing with alkaline solutions such as NaOH, NH₃.¹⁸⁻²⁰ It was found that OD is responsible for the excellent solubility and several other properties such as electroactivity and fluorescence of GO.^{18-19, 21} It is also well known that OD greatly influence the catalytic activities of GO.²² This thesis studied the effect of OD on cure kinetics of epoxy matrix.

The coupled mechanical properties and cure chemistry will provide new knowledge relating to interfacial interactions, interphase properties and mechanisms responsible for the strengthening and toughening behaviour of graphene-polymer nanocomposites.

Although graphene has exceptional electrical conductivity, GO is typically insulating because of presence of sp³ hybridized carbons and oxygen functional groups.²³ GO also has high dielectric constant.²⁴ These properties were exploited here using GO as dielectric spacer material in supercapacitors for the first time.

Graphene has been attracting interest as an ideal component in gas sensors due to its excellent detection sensitivity and long-term stability arising from unique properties of graphene such as large specific surface area, extraordinary mobility of carriers etc. Moreover, the sensitivity and selectivity of graphene can be engineered by creating defects or introducing dopants in to its surface.²⁵ In this thesis, we synthesised alkali metal ion doped GO using Cs₂CO₃ to enhanced its gas sensing ability. We found that the fabricated conductometric sensors are highly sensitive for NO₂ gas at room temperature.

1.2 Aims and Objectives

The main aim of this research was to achieve a fundamental understanding of the reinforcing behaviour of graphene oxide in epoxy nanocomposites by correlating its underlying mechanisms with the interface microstructure. This thesis investigated the influence of graphene oxide on the cure and chemical reaction mechanisms of epoxy and overall mechanical and thermal properties of epoxy nanocomposites. In addition, GO and doped-GO based electronic devices were fabricated and characterised for supercapacitors and gas sensing applications. Some specific objectives of this thesis are listed as follows:

- Synthesis of adequate amounts of well characterized GO required for composites

- Fabricate new GO-epoxy nanocomposites with excellent mechanical and physical properties
- Investigate influence of GO on the cure and chemical reaction mechanisms of epoxy nanocomposites and the interphase properties
- Understand the underlying reinforcing mechanisms of GO-polymer nanocomposites
- Fabrication and characterization of GO based super-capacitors
- Structural modification of GO and fabrication of gas sensing devices using doped-GO materials.

1.3 Thesis Outline

This thesis consists of 7 chapters and specific objectives and outline of each chapter are given below.

Chapter 2 presents a comprehensive literature review of graphene and its nanocomposites. Areas covered include graphene, graphene oxide and their properties and applications, fabrication, properties and applications of graphene-polymer nanocomposites. Overview of toughening and toughening mechanisms of epoxy, polymer nanocomposites interface and interphase are also included. Finally cure kinetics and experimental evaluation techniques of epoxy curing process are presented.

In chapter 3, the effect of graphene oxide on the property enhancement of epoxy matrix is specifically studied. Mechanical, thermal and cure properties are evaluated with the variation of GO weight fraction.

In Chapter 4, the analytical approach for *in situ* monitoring of cure process of epoxy matrix and the effect of GO on cure kinetics are presented. The study is done by using Fourier transform infrared emission spectroscopy and is compared with DSC study. This chapter further presents the effect of oxidative debris (OD) on the curing process.

Chapter 5 presents the fabrication and performance of GO based supercapacitors. Finally, the gas sensing properties of Caesium doped GO (Cs-GO) results are presented in Chapter 6.

The main conclusions resulting in this project are summarised in Chapter 7. Possible future work of research is also included.

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2 Literature Review

This chapter introduces the background information relevant to graphene and graphene-polymer nanocomposites. The overview of the first part of chapter discusses recent advances in synthesis, properties and applications of graphene, followed by fabrication and properties of graphene-polymer nanocomposites. The second part of the chapter summarizes the kinetics and cure process of epoxy resins, how they can be evaluated with available techniques and theory behind the evaluation techniques.

2.1 Graphene

Graphene is a single atom thick sheet of sp^2 hybridized carbon atoms which are covalently bonded to three others with a carbon–carbon bond length of 0.142 nm, forming a hexagonal ring structure. Graphite, a 3-dimensional (3D) layered crystal lattice structure, is formed by stacking parallel 2-dimensional (2D) graphene sheets as is shown in **Figure 2.1**. The adjacent graphene sheets in graphite are held together by weak van der Waals forces with the separation distance of 0.335 nm from each other. P_z orbitals of the carbon atoms can overlap most effectively when they are parallel; thus the graphene sheet has the lowest energy when it is completely flat. The π orbital is distributed over the entire graphene sheet making it thermally and electrically conductive.¹⁻³ Graphene is the basic building block of all other graphitic forms of carbon such as nanotubes (CNTs) and fullerenes (**Figure 2.2**).

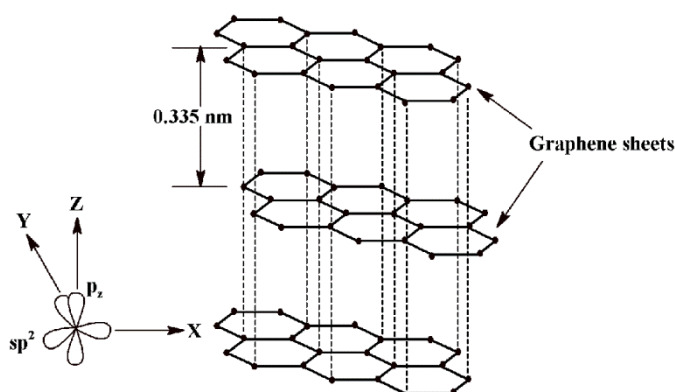


Figure 2.1. Layered structure of graphite showing the sp^2 hybridized carbon atoms tightly bonded in hexagonal rings.

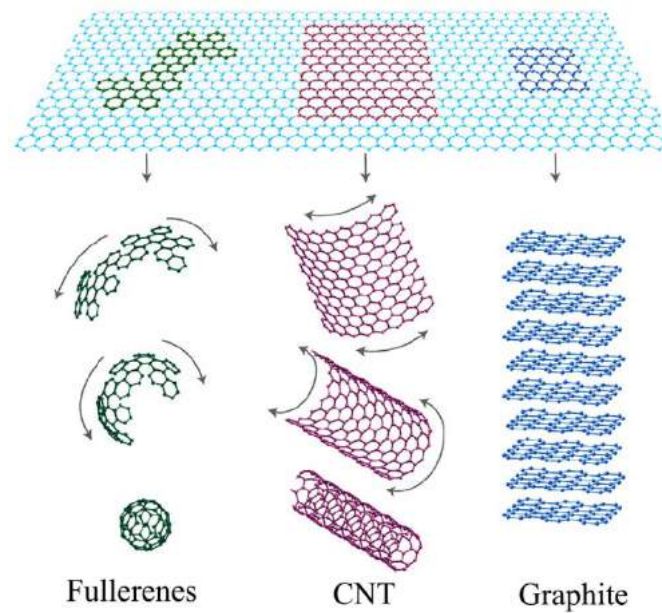


Figure 2.2. Basis of all graphitic forms. Graphene is a 2D building material for other dimensionalities of carbon materials.⁴⁻⁵

Based on both theoretical calculation and experimental observation, it was believed that 2D materials did not exist without a 3D base. Theoretical calculations showed that graphene is the least thermodynamically stable structure until about 6000 carbon atoms and becomes the most stable one when its size is larger than 24000 carbon atoms.⁶ Various attempts were made to synthesize graphene, but it was not until 2004 that ground-breaking research by Andre Geim and Konstantin Novoselov (Nobel Prize winners in Physics, 2010) of the University of Manchester led to the isolation of a single sheet of graphene which was prepared by using the scotch tape method on the top of a silicon wafer.² Today, graphene is the subject of much research in the scientific community; further, it can be utilized in several industrial applications because of its outstanding electronic, optical, thermal and mechanical properties. For example, monolayer graphene has high optical transparency (as seen in **Figure 2.3(a)**)⁷ due to capability of absorbing ~2.3% white light which makes graphene an important material for applications and development of optical electronic materials. **Figure 2.3(b)** illustrates the highly ordered hexagonal structure of single-layer graphene sheet observed by an aberration-corrected transmission electron microscope (TEAM).⁸

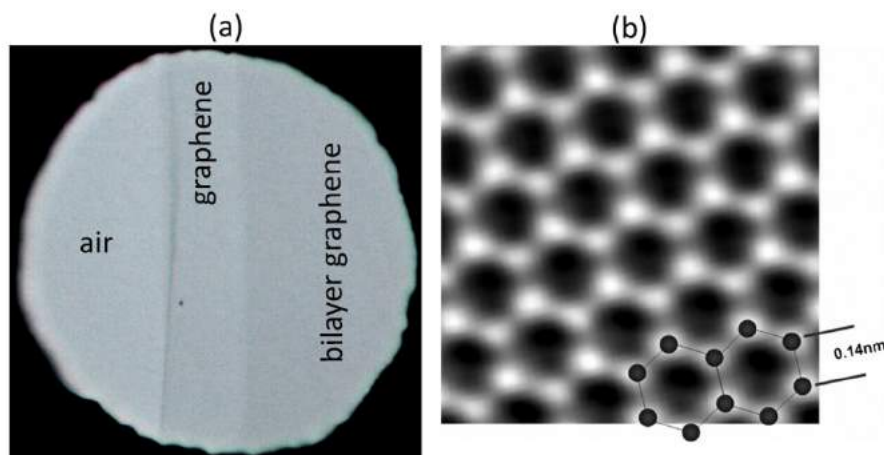


Figure 2.3. (a) A single sheet graphene can be visualized by eye⁷, (b) TEM image of a graphene sheet illustrating the crystalline lattice.⁸

2.1.1 Synthesis of Graphene

Since the first demonstration of monolayer graphene was reported, much effort has been devoted to develop methods of attaining high quality pristine graphene due to its excellent in- plane mechanical, structural, thermal and electrical properties. However, exfoliation of graphite to monolayer graphene sheet is of paramount importance to accomplish these excellent properties. Graphene has very large surface area and is densely packed due to van der Waals interactions. Therefore, unless they are well separated from each other, graphene layers tend to restack and to re-aggregate. Thus, a key challenge in synthesis of bulk quantity graphene is prevention of aggregation. In general, graphene synthesis can be carried out by four different methods: Mechanical exfoliation, chemical vapour deposition (CVD), epitaxial growth and chemical reduction of graphene oxide.^{2, 4}

Mechanical exfoliation is a simple peeling process of highly-ordered pyrolytic graphite (HOPG) by a scotch tape. Thin flakes left on scotch tape are composed of monolayer or a few layers of graphene.⁹⁻¹⁰ This method generates pristine graphene but this approach is limited by its low production. Physical exfoliation is a method which produces high quality and un-oxidized monolayer graphene and this approach is desirable where it is required to maintain the graphene structure.⁹ In this approach, the energy required for exfoliation is balanced by the solvent-graphene interactions through surface energy match of solvent and graphene. Surfactants such as sodium dodecylbenzene sulfonate (SDBS) and sodium cholate have been used to exfoliate graphite in water to graphene. The aggregation of monolayer graphene was

prevented by large potential barrier caused by the Coulomb repulsion between surfactant coated sheets.¹¹⁻¹² Graphene sheet can be made from graphite intercalated compounds (GICs), commonly known as expandable graphite. GICs are made by incorporating small molecules between the layers of graphite or by the non-covalent attachment of molecules or polymer onto the sheets to prevent agglomeration in to graphite. The expandable graphite is then expanded at elevated temperature such as 900°C to obtain the expanded graphite (EG). Li et al¹³ reported the synthesis of high quality monolayer graphene sheets through the continuous exfoliation-reintercalation-expansion processes of graphite in organic solvents. The graphene sheets exhibited high electric conductance at room temperature.

Chemical vapour deposition (CVD) is a substrate-based method that involves the diffusion of the carbon into a transition metal substrate at the growth temperature followed by a precipitation of carbon out of the bulk metal to metal surface upon cooling. Typically, Ni or Co films are used as substrate and methane as the feeding gas. The deposition process is carried out in a CVD chamber under vacuum at temperature below 1000°C. Upon cooling the substrate, the solubility of the carbon on the substrate decreases and a thin film of carbon precipitate on the surface to form graphene sheets. The thickness of the graphene layers is controlled by the cooling rate and the concentration of carbon dissolved in the Ni substrate. However, it is rather difficult to control the film thickness and the requirement of expensive substrate materials is another major disadvantage of CVD method that limits its application for large-scale production.^{2, 14-15} Interestingly, Qu et al. demonstrated a modified CVD process for the synthesis of nitrogen doped graphene films using nitrogen containing gas mixture as feeding gas.¹⁶

Epitaxial growth is another substrate-based method where monolayer graphene is grown on Silicon carbide (SiC) by the high temperature reduction of SiC substrate. High thermal treatment of SiC under vacuum results in sublimation of the silicon atoms and the formation of graphene by reorganization and graphitization of the carbon-enriched surface. A number of physical properties differ significantly between epitaxially grown and mechanically exfoliated graphene due to the influence of interfacial effects in epitaxial graphene.¹⁴⁻¹⁵

Chemical conversion of graphite into graphite oxide and subsequent reduction has become a viable route to synthesise graphene in considerable quantities. Graphite

oxide is usually synthesized through the oxidation of graphite using oxidants based on Hummers method.¹⁷ Further details of synthesis and properties are discussed in the section 2.2.1. GO reduction can be done by either chemical or thermal reduction approach. Chemical reduction of GO sheets has been performed with several reducing agents such as hydrazine¹⁸⁻¹⁹, sodium borohydride²⁰. Thermal reduction utilizes heat treatment to remove the oxygen functional groups from GO surfaces.²¹

Apart from these main synthesis approaches, the Dai research group have recently fabricated graphene nanoribbons (GNRs) with well controlled dimension through controlled unzipping of carbon nanotubes (CNTs) using an argon plasma etching method.²² Shimizu and co-workers produced GNRs through oxidation and longitudinal unzipping of CNTs using conc. H_2SO_4 and KMnO_4 followed by three steps annealing treatment to completely remove oxygen from GNRs.²³ Total organic synthesis approach from precursor monomers has been reported as a possible route to synthesize graphene or GNRs.²⁴⁻²⁶ **Table 2.1** summarizes the basic synthesis route, advantages and disadvantages of main graphene synthesis approaches.¹⁵

2.2 Graphene oxide (GO)

Graphene oxide (GO) is the highly oxidized derivative of graphene possessing various oxygen-containing functional groups such as carbonyl, hydroxyl, epoxy and carboxyl. These groups, found on both the edge and basal plane of the nanosheets, as schematically shown in **Figure 2.4**, convert the sp^2 -bonded graphene network to a combination of sp^2 - and sp^3 - hybridized carbon. These introduced sp^3 defect sites distort the intrinsic conjugated π system and lower overall strength and conductivity. Nevertheless, these groups make graphene oxide highly attractive as a multifunctional material for a wide range of applications, as it can be readily modified with several functional groups.²⁷

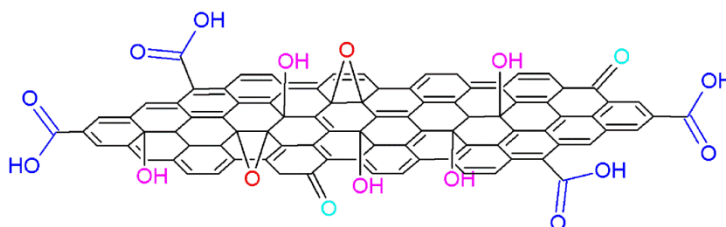
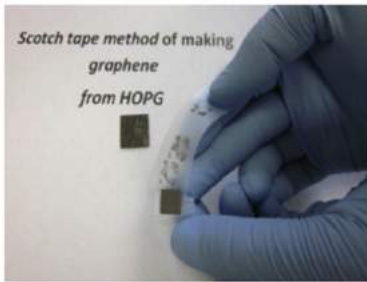
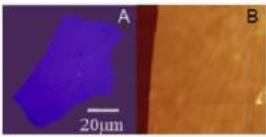
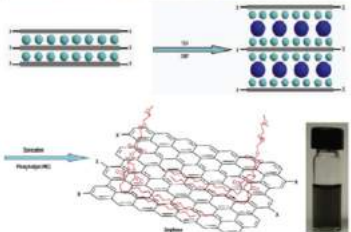
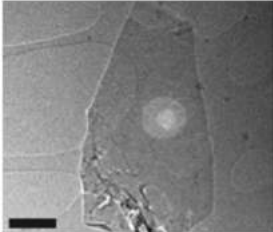
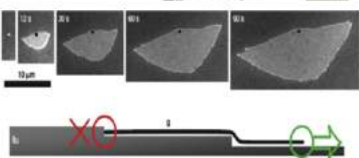
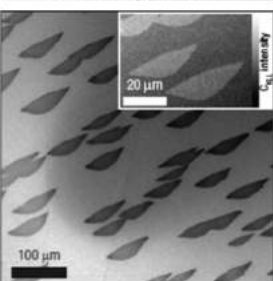
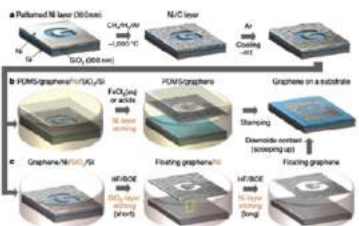
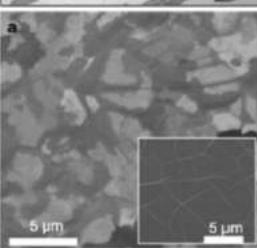
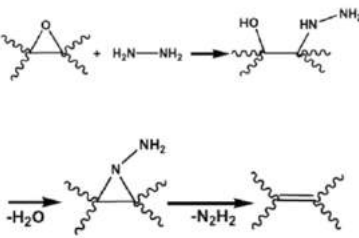
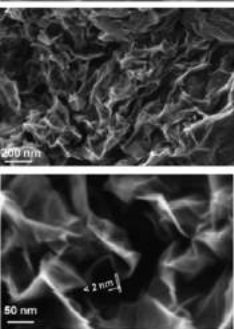


Figure 2.4. Schematic structure of graphene oxide (Please note that this is only an example, there is no definitive structure of GO, as no stoichiometric definition so far).

Table 2.1. Synthesis of graphene.¹⁵

Method	Figure/illustration	Images	Advantages	Disadvantages
Mechanical cleavage			No defects	Neither scalable nor capable for mass production
Solution exfoliation			Less defects	Low efficiency and hard to control the number of layers
Epitaxial growth			No defects for every single graphene island	Discontinuous
CVD			Compatible with the current CMOS technologies	High cost and complex transfer process
Reduced GO			Low cost and suitable for mass production	The majority of defects can be removed

2.2.1 Synthesis

Almost 150 years ago, Brodie prepared highly oxidized graphite oxide with a C/O/H ratio of around 2.2/1/0.8 through the oxidation of graphite using potassium chlorate and nitric acid mixture.^{2, 28-29} The Brodie method was modified by Staudenmaier who replaced the oxidizing agent by a mixture of sulfuric acid and nitric acid.^{2, 29} In 1958, Hummers and Offeman reported less hazardous and more

efficient method using a water-free mixture of sodium nitrate, potassium permanganate and concentrated sulfuric acid, the method most commonly used today.¹⁷ Recently, Tour and co-workers improved the Hummers' method by excluding the NaNO_3 , increasing the amount of KMnO_4 , and performing the reaction in a 9:1 mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$. The method has advantages of its simpler protocol, higher yield, higher efficiency, fewer defects and no toxic gas evolution during oxidation.³⁰

Flake graphite is the most common source of graphite used for oxidation. This naturally occurring flake graphite is purified to remove heteroatom contamination and contains numerous localized defects which may serve as seed points for the oxidation process. However, the elucidation of the precise oxidation mechanism remains an ongoing challenge due to the complexity of flake graphite and the defects that are inherent as a result of its natural source.⁶ **Figure 2.5** shows schematic presentation of synthesis of GO.³¹

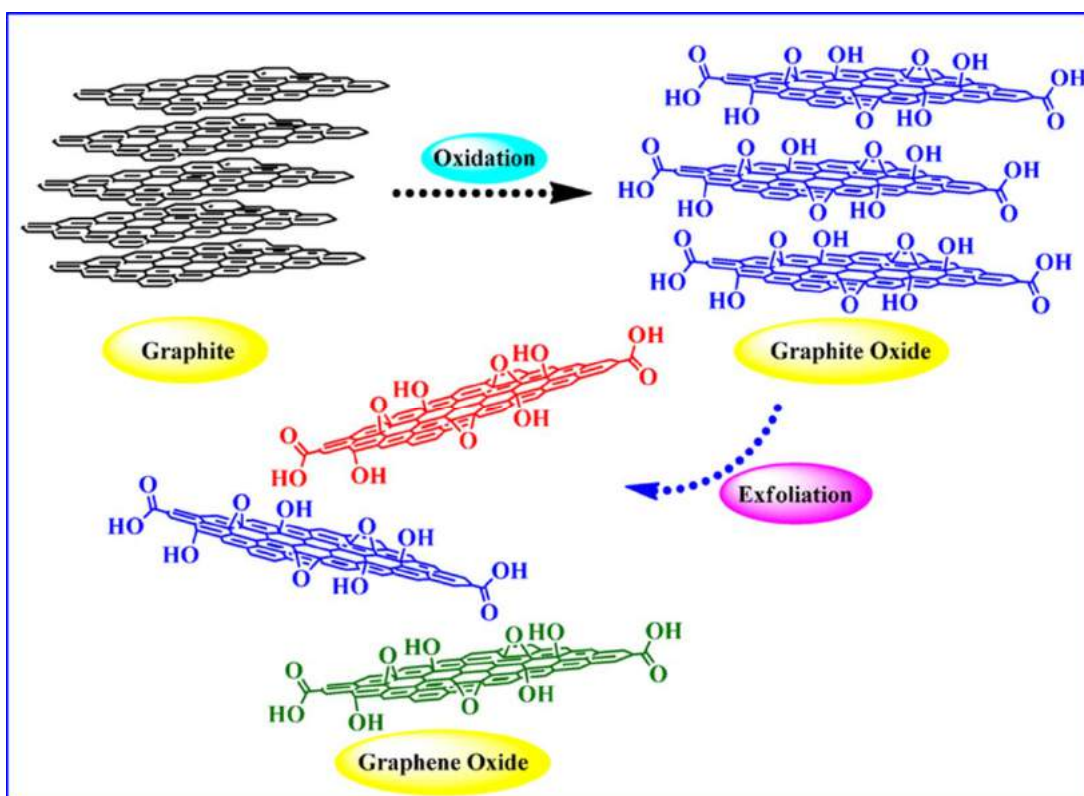


Figure 2.5. Synthesis of graphene oxide.³¹

2.2.2 Structure

The precise chemical structures of GO remains the subject of debate over the years for major reasons of the complexity of material as its amorphous, berthollide

character and the lack of precise analytical characterizing techniques. Moreover, it has been shown that the structure of GO varies depending on oxidation conditions, the graphite precursor material employed and workup treatments. Even with these obstacles, several structural models have been proposed to understand the structure of GO, as shown in **Figure 2.6**.

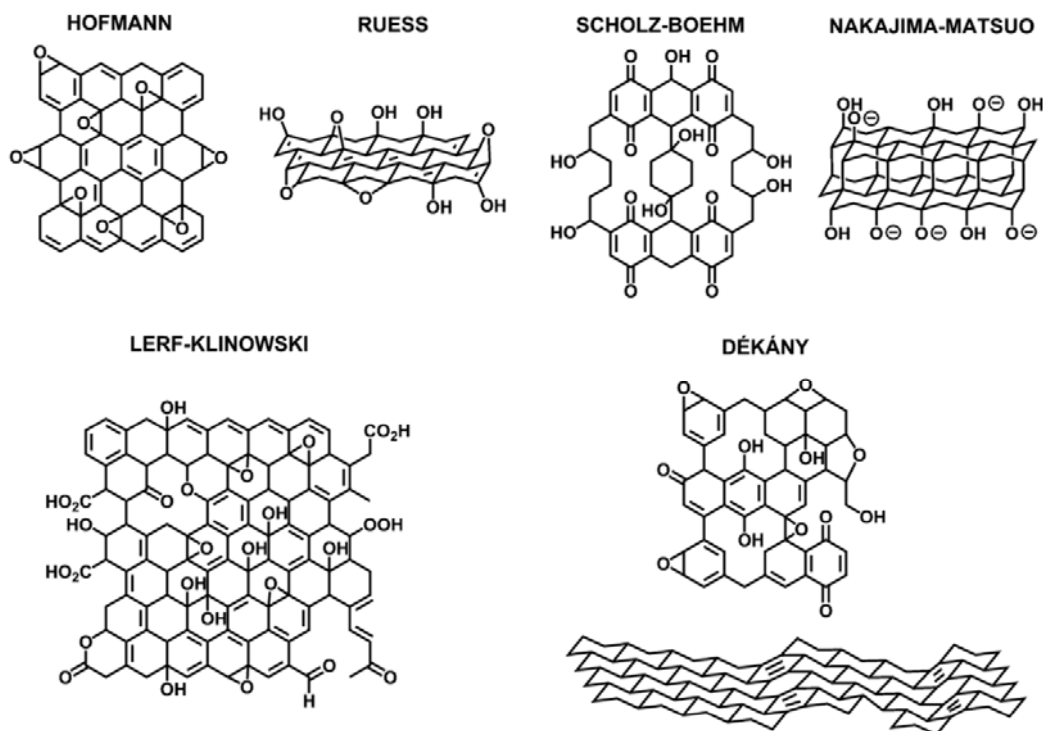


Figure 2.6. Summary of structural models of GO that have been proposed.^{6, 32}

Hofmann and co-workers proposed a model which consists of epoxy groups spread across the basal planes of graphite with a net molecular formula of C_2O .^{6, 33} In 1946, the Hofmann model was modified by Ruess who incorporated hydroxyl groups in to the basal planes considering the H content of GO. Further, he has altered sp^2 hybridized basal plane structure into sp^3 hybridized system.⁶ Both Scholz and Boehm and Nakajima and Matsuo also suggested valuable structural models to understand the chemical structure of GO. Scholz and Boehm's model consists of regular quinoidal species in a corrugated backbone where they have completely removed the epoxide and ether groups from the carbon structure.^{6, 34} The Lerf–Klinowski model has been the most well-known and widely adopted model which has been based on a nonstoichiometric and amorphous structure model. The model relied on experimental studies on ^{13}C and ^1H NMR and X-ray diffraction.³⁵ Their model has defined two different regions; these are either predominantly aromatic regions with un-oxidized

benzene rings and second; regions with aliphatic six-membered rings. The relative size of the regions is determined by the degree of oxidation. In this model, GO basal plane is decorated with hydroxyl and epoxide groups (or 1,2- ethers) which are very close to one another and layers terminated with C-COOH and C-OH groups. Only carbon atoms attached to hydroxyl groups are in slightly distorted tetrahedral configuration, resulting in some wrinkling of the layers.

The functional groups are attached both above and below the carbon grid forming a negatively charged layer of oxygen atoms that prevent nucleophilic attack on carbon atoms.³⁵ Their ¹H NMR study further indicated that the water molecules are strongly bound to the basal plane of GO through hydrogen bonds (**Figure 2.7**) which can be the key factor in maintaining the stacked structure of GO.³⁵⁻³⁶

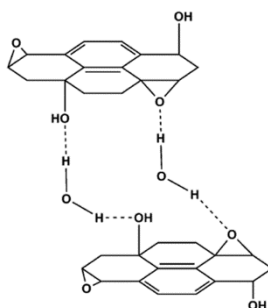


Figure 2.7. Proposed hydrogen bonding formed between GO and water.^{6, 36}

Though the Lerf–Klinowski model remains unchanged over years, Dékány et al. has revived and updated Ruess and Scholz-Boehm models based on their FTIR and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopic studies.³⁷ They have found that the signal at 1714 cm^{-1} in IR spectrum of GO was indicative of single ketones and/or quinones and not indicative of carboxylic groups. They have included phenolic groups into the bulk structure by which the planar acidity can be easily explained. The model also exhibits a carbon skeleton consisting of two distinct domains trans-linked cyclohexane chairs combined with tertiary alcohols and ethers and ribbons of flat hexagons of keto/quinoidal species. A slight tilting between the boundaries of these regions can be the possible basis for the wrinkled structure observed by TEM.³⁷

As a conclusion, it has been a challenge to determine the precise molecular structure of GO due to its non-stoichiometric chemical composition. The variation in degree of oxidation, which can be due to the difference graphite source and oxidation protocol can cause substantial changes in the structure and properties of GO. Some

theoretical studies showed that the exact identity and distribution of oxygen functional groups depends strongly on the extent of coverage. It also revealed that the ratio of epoxides to alcohols increases with increasing degree of oxidation and complete oxidation is less thermodynamically favoured than partial oxidation.³⁸

2.3 Doping

Doping graphene with other chemical elements can modulate its electronic and quantum transport properties for device applications like sensors, electronic display panels, supercapacitors etc.³⁹⁻⁴⁰ Intercalation with dopants improves its electrical conductivity through the formation of charge transfer complexes.⁴¹ The changes in properties depend on the nature of the dopants, their location and their concentration. Substitution of carbon atoms in the graphene cluster with heteroatoms such as N, Br, Cs etc., could produce graphene with electrons or holes, exhibiting n-type or p-type behaviours. Several methods have been reported to synthesise nitrogen doped (N-doped) graphene such as introducing doping gas (NH_3) into the CVD system during the graphene growth or treatment of graphene or GO with NH_3 /urea.^{40, 42-44} Wei and co-workers synthesised N-doped graphene by a CVD method where they have introduced mixture of CH_4 and NH_3 gases during the growth process.⁴⁴ The N content can be controlled by the ratio of NH_3 and CH_4 . XPS analysis indicated that N atoms are in the three different bonding characters i.e.; graphitic, pyridinic and pyrrolic as shown in **Figure 2.8**. Mou et al. and Sun et al. have reported N-doped graphene sheets with the nitrogen level of ~ 10 atoms% using GO and urea^{40, 42}. Mou et al have produced highly electrical conductive N-doped GO using solid-state reaction while Sun et al. synthesized N-doped GO exhibiting excellent capacitive behaviours, superior cyclic stability and columbic efficiency.

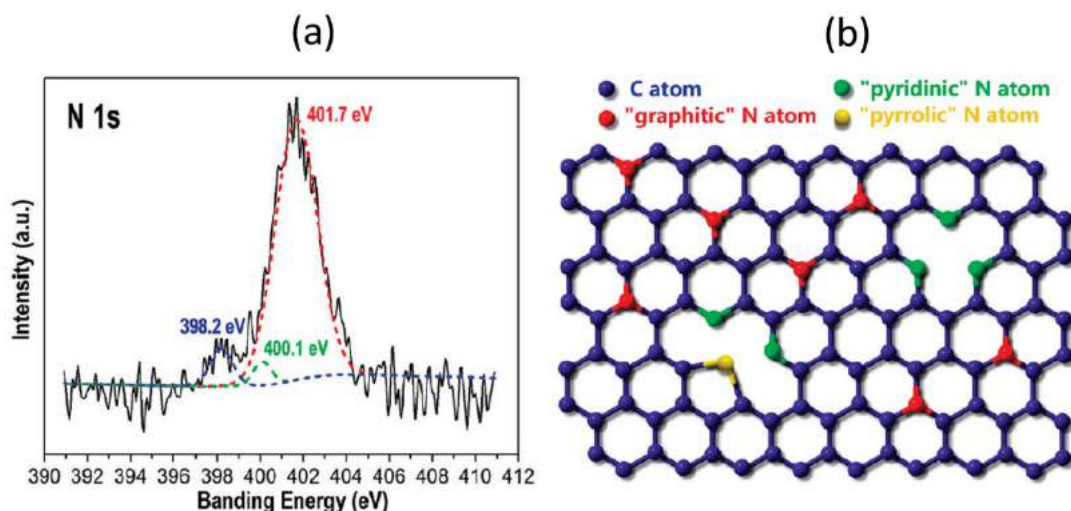


Figure 2.8. (a) XPS N1s spectrum of the N-doped graphene (b) schematic representation of the N-doped graphene.⁴⁴

Recently, studies on alkali metal-doped GO have also been reported.⁴⁵⁻⁴⁶ Liu et al. reported Caesium-neutralized GO (Cs-GO) as an excellent electron extraction layer for polymer solar cells. They observed that the peripheral -COOH groups of GO can be neutralized by Cs_2CO_3 and could change the work function of GO. In our work, we have found that Cs-GO can be used as a highly NO_2 sensitive gas sensors which is detailed in chapter 6. Gierz et al., demonstrated p-type doping of an epitaxial growth graphene layer by doping with gold, bismuth and antimony.⁴⁷ Brominated graphene has been reported via vapour-phase bromination by Li and co-workers.⁴⁸ Both ionic Br and covalently bonded Br were introduced simultaneously and increased with duration of bromination. The ionic bonds can enhance the electrical conductivity of graphitic material by adding either electrons to its conduction band or holes to the valence band; while the covalent bonds can weaken the carrier concentration and thus shift some of the carbon atoms away from the highly planar structure of pristine graphite, decreasing the electrical conductivity.

2.4 Properties and Applications of Graphene and Graphene Oxide

Graphene can be utilized for applications in electronics, semiconductors, gas absorbers, sensors, solar cells, fuel cells, optic devices and composites due to their outstanding properties. The most promising applications of graphene rely on their transparency and very high conductivity. Single layer graphene has unique electronic structure and properties with zero band gap, high carrier mobility and

concentration, and shows nearly ballistic transport at room temperature. Single layer graphene also shows room-temperature ambipolar characteristics, quantum Hall effect.⁴⁹⁻⁵⁰ These unusual properties have made graphene suitable for applications in electronics.⁵¹⁻⁵² Graphene's exceptional electrical properties combined with its 2D structure with high specific surface area (calculated value $\sim 2630 \text{ m}^2\text{g}^{-1}$) make graphene an efficient gas absorber to fabricate next-generation sensors.⁵³ However, GO sheets are typically insulating, exhibiting sheet resistance (R_s) values of about $10^{12} \Omega/\text{sq}$ or higher due to the extensive presence of sp^3 hybridized carbon cluster, the high density of electronegative oxygen atoms bonded to carbon, and other defects.^{15, 54} Chemical or thermal reduction of GO can make GO electrically conductive. Heat treatment of GO decomposes the oxygen functionalities and restores the sp^2 carbon clusters which leads to higher electrical conductivity.^{15, 55} Wang et al., reported reduction of GO films chemically followed by thermally, decreased the R_s value by approximately four orders of magnitude.⁵⁵ Another study reported that fully reduced GO has oxygen content and sp^2 concentration of $\sim 8\%$ and 80% , respectively. It found that presence of residual oxygen significantly impedes the carrier transport. Further, the study reveals that transport at the initial stages of reduction is dominated by hopping and tunneling among sp^2 clusters and at later stages of reduction by percolation as original sp^2 clusters are connected by newly formed small domains as shown in **Figure 2.9**.⁴⁹

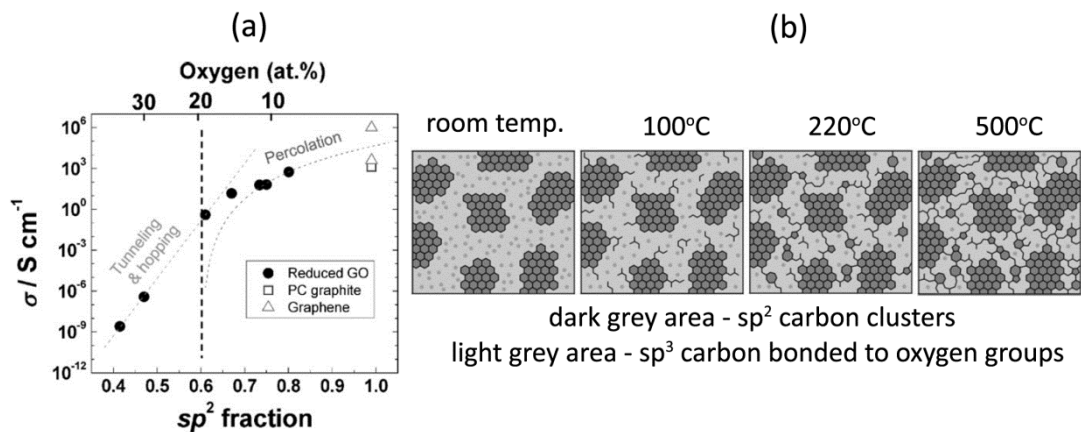


Figure 2.9. (a) Conductivity of thermally reduced GO as a function of the sp^2 carbon fraction. Vertical dashed line indicates the percolation threshold at sp^2 fraction of ~ 0.6 . (b) schematic structural model of GO at different stages of reduction by thermal annealing.⁴⁹

Young's modulus and intrinsic strength of free standing monolayer graphene were measured as 1.0 TPa and 130 GPa, respectively, using nanoindentation in AFM.⁵⁶ In a separate study, mechanical properties of GO sheets were measured using AFM and found that effective Young's modulus of monolayer GO (thickness of 0.7 nm) was 207 ± 23.4 GPa. The attachment of oxygen functional groups alters the perfect 2D structure of graphene which caused a much lower strength of GO sheet compared to pristine graphene.⁵⁷ Molecular simulations studies showed that the Young's modulus of GO is strongly dependent on the degree of functionalization and the molecular structure of the functional groups as shown in **Figure 2.10**. Changes in molecular structure and binding energy with the presence of functional groups, cause the graphene sheets to become unstable and consequently degrade the elastic properties of GO sheets.⁵⁸ Similar to mechanical and electrical properties, the thermal conductivity of GO is much lower than pristine graphene due to the presence of defects and disorders. The thermal conductivity of the single layer of defect free graphene and reduced GO was reported in the range of $4.84 \times 10^3 - 5.30 \times 10^3$ W/mK and $0.14 - 2.87$ W/mK, respectively.¹⁵ A unique combination of excellent electrical, thermal and mechanical properties has made graphene a multi-functional reinforcement for polymers and open a new avenue for developing high strength light weight structural polymer composites for automobile, aerospace, thermally conductive support in the electronic industry for thermal management, packaging for food, medicine, electronics and beverages.²

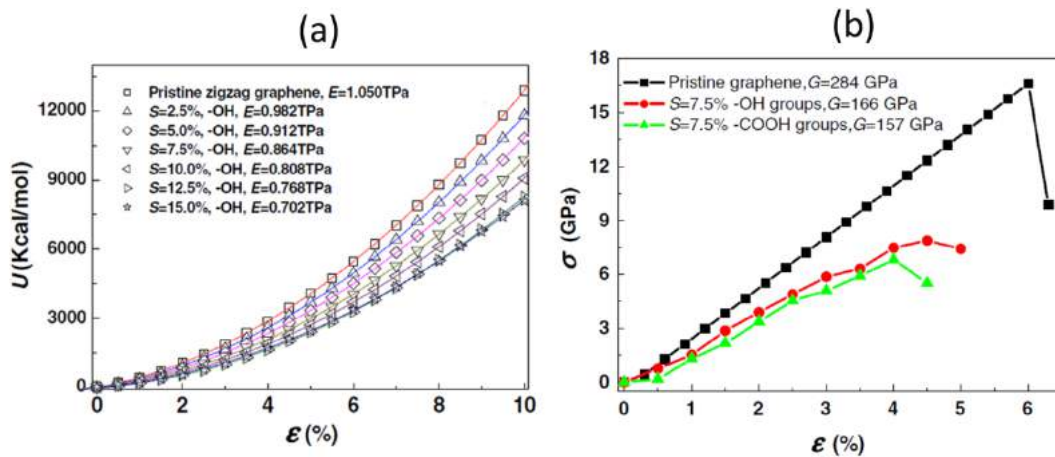


Figure 2.10. (a) Effect of degree of functionalization, S , on Young's modulus of graphene sheets, U =strain energy, ϵ (%) = tensile strain (b) effect of different functional groups on shear stress –strain curves.⁵⁸

2.5 Oxidative Debris (OD)

As yet, the exact chemical structure of GO remains imprecise and it is only recently that the Rourke research group have found that GO is a highly heterogeneous material that consists of poorly oxidised graphene sheets and highly oxidised graphene debris.⁵⁹ This oxidative debris (OD) can be defined as highly oxidised small, fulvic acid-like fragments strongly adsorbed on the graphene matrix by π - π stacking, hydrogen bonding, and van der Waals interactions.⁶⁰ The polyaromatic oxidative fragments are generated during the oxidation of graphite. However, this debris is sufficiently large to be insoluble and adhered strongly to the graphitic surface. Schematic representation of as prepared GO (aGO) is shown in **Figure 2.11**.

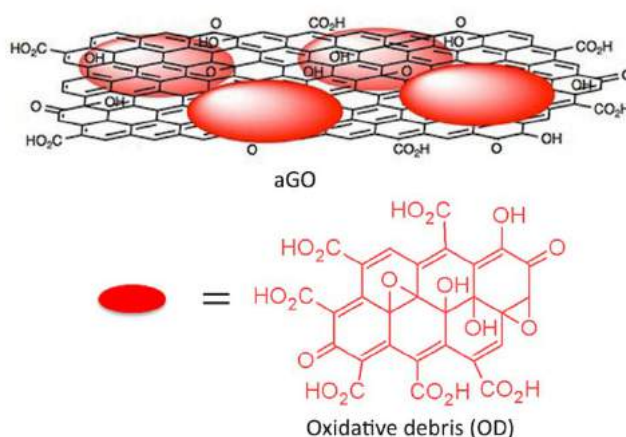


Figure 2.11. Schematic representation of as-prepared GO (aGO): large oxidative functionalized graphene-like sheets with surface bound debris.⁵⁹

In literature, it has been reported that treatment with alkaline solutions such as aqueous NaOH or NH_3 was necessary to remove the adhered OD. The fraction of OD in as-prepared GO is ~14-30%.⁵⁹⁻⁶¹ Further, it was discovered that the majority of the oxygen functional groups found in bulk GO are actually in these smaller fragments. The OD is responsible for the excellent solubility of GO and as a result, OD-free-GO cannot be re-suspended in water. It is also reported that much of the fluorescence of GO is attributable to the OD fragments.^{59-60, 62} The inherent electro-chemical activity (the inherent reduction of the material itself) of GO mostly resides in the OD as separation of OD corresponded to a net reduction in the inherent electroactivity of GO.⁶³ Coluci et al. found that OD play an important role on the non-covalent interaction of GO with aromatic compounds where OD is responsible for obstructing

adsorption sites on the GO and removing OD increases adsorption capacity of GO by 75%.⁶¹ OD in GO acts as a compatibilizing surfactant which can be beneficial in producing polymer nanocomposites with a good dispersion as well as a strong interface between GO and polymer matrices.⁶⁴ This thesis will reveal for the first time, the simple and easy autoclave technique to isolate OD instead of complex base washing method and, further, this thesis will evaluate the effect of OD on cure process of epoxy system in chapter 4.

2.6 Graphene-Polymer Nanocomposites

Graphene-based polymer composites have shown very exciting results in improving electrical conductivity at a very low percolation threshold, increase in strength and elastic modulus, high thermal conductivity and stability, and reduced permeation of gas molecules. A comprehensive review on fabrication and properties of graphene-polymer nanocomposite can be found in our paper published in “Graphene” which is included at the end of this chapter.

However, to get full advantage of graphene properties in the composites, integration of individual graphene layers in polymer matrices is crucially important. Moreover, the final properties of the composite depend on interfacial interaction and stability of interphase, wrinkle structure of graphene etc.

2.6.1 Polymer Nanocomposites Interface

In polymer matrix composites, the interface, the immediate contact surfaces between the reinforcing phase and the bulk phase is paramount to the overall performance of the composite. The interactions between the reinforcing phase and the bulk phase occur via interface and these interfacial interactions and adhesion play a key role in the stress transfer from the bulk phase to the reinforcing phase and consequently improvements in mechanical properties. The better the interfacial adhesion/interactions, the greater load it can withstand before interface failure. In the case of lower interfacial adhesion, the strength of the interface decreases and leads to lower load transfer between the bulk and the reinforcing phase. Therefore, strong adhesion and interactions between bulk polymer and the reinforcing phase is essential for improved strengthening of composites. Interface can be experimentally studied by both Raman spectroscopy and AFM.⁶⁵⁻⁶⁹

Characteristic Raman bands are found to be shifted proportionately with applied stress which enables stress transfer to be probed between the matrix and filler and to determine the extent of filler-polymer interfacial interactions. Both G and 2D bands have been used to follow up the stress transfer. It has been reported that G band is linearly decreased under tension and increased under compression.^{65, 68} The study of the Koratkar group found large debonding strains of ~7% graphene in PDMS with the G peak shift rate of ~2.4 cm⁻¹/composite strain% occurs. In comparison, SWCNT composite showed a relatively low rate of ~0.1 cm⁻¹/composite strain%, suggesting enhanced load transfer effectiveness of graphene.⁶⁵ In contrast, Gong et al. found that interfacial shear stress between graphene and polymer is much lower than that between CNTs and polymer.⁶⁸ The lower interfacial shear stress was attributed to the poor interface adhesion.

Unlike graphene, GO has weak 2D band and the broad G band. This makes it difficult to use these bands to monitor deformation of GO-based nanocomposites. Hence, the shift of the Raman D band has been utilized to follow the interfacial stress transfer between the polymer and GO reinforcement. Similar to G band, Raman D band at ~1335 cm⁻¹ downshifted linearly with an average rate of 8 cm⁻¹/strain % as the nanocomposites were strained.⁶⁶

AFM topography and force curves are also useful techniques to evaluate the interface. Benli et al. have used the AFM colloidal probe method to measure the adhesion and interaction forces between polymer (alginate) and mineral fillers. Surface roughness has a significant impact on the measured adhesion force resulting in very low values of adhesion for the relatively rough surfaces.⁶⁹ Direct characterization of the relative strength of the interfacial attractive forces between GO nanoparticles and the polymer matrix on the nanoscale using AFM technique found that GO-PVA has higher interfacial strength compared to GO-PMMA.⁶⁷

2.6.2 Polymer Nanocomposites Interphase

The region between contact surfaces of the filler and the polymer matrix is known as the interphase.⁷⁰ Physical and mechanical properties and even chemical composition of the interphase region are different from the bulk polymer matrix.⁷⁰⁻⁷² In general, the overall performance of a polymer composite strongly depends on the quality and the stability of the interphase region formed. For example, an interphase

that is stiffer than the surrounding polymer would give the composite less fracture resistance but it would be strong and stiff. On the other hand, the softer interphase would result in lower overall stiffness and strength, but greater resistance to fracture.⁷³ Moreover, the morphology and the size of the interphase will also determine the mechanical behaviour of composite. For example, the thickness of the interphase needs to be optimized in order to obtain both higher strength and improved toughness of composites. Force modulation AFM and nanoindentation are being used to determine the interphase and its properties.^{71, 74} AFM phase imaging is another highly useful approach to determine the thickness and relative stiffness of interphase because it involves much lower interaction forces between the probe and the sample than force modulation or nanoindentation.⁷³ The result showed that the interphase in the model composite (glass fibre/epoxy) is softer than bulk matrix with a thickness of 2.4-2.9 μm .⁷³ Another study used combined nanoDMA and scanning probe microscopy technique to measure viscoelasticity distribution on the cross sections of unidirectional carbon fibre composites. It has been found that the dimension of the interphase is 118 ± 3 nm based on a statistical estimate of the pixel count as a function of the storage modulus (**Figure 2.12**).⁷²

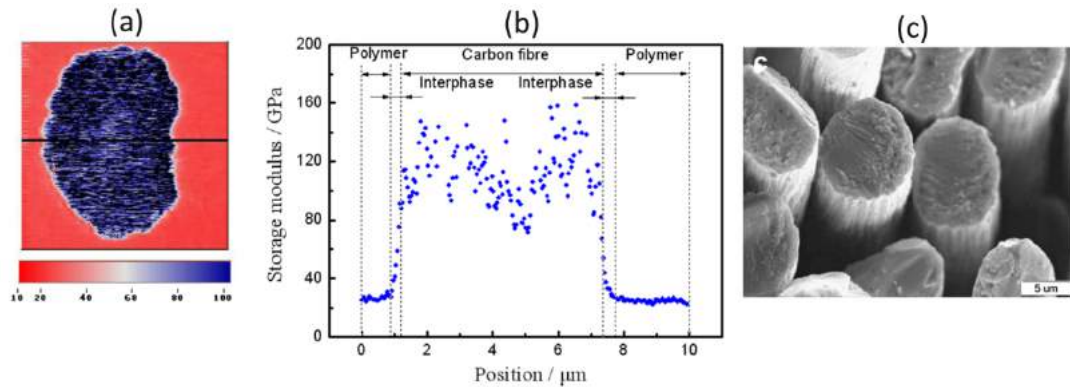


Figure 2.12. (a) Storage modulus map of a T300 carbon fiber reinforced epoxy resin composite sample with an area of $10 \mu\text{m} \times 10 \mu\text{m}$. (b) Line scan through the center of (a), showing a storage modulus gradient between the polymer matrix and the fiber (c) SEM image of cross sections of T300 carbon fibers.⁷²

2.6.3 Fracture Toughness of Polymer Nanocomposites

The fracture toughness (K_{IC}) is a material property which measures the resistance of a material to the propagation of a crack. It is measured by loading a sample containing a deliberately introduced crack (length $=2c$) or a surface crack

(length = c), recording the tensile stress (σ^*) or bending load (F^*) at which the crack suddenly propagates. The quantity (K_{1C}) is then calculated;

$$K_{1C} = Y\sigma\sqrt{\pi c} \quad (1)$$

It is essential that the crack should be sharp. Y is a geometric factor that depends on details of the sample geometry (**Figure 2.13**).⁷⁵ K_{1C} is independent of the different sample geometry, test method if properly conducted and should give the same value for any given material.

K_{1C} is related to the energy release rate G_{1C} which is defined as the amount of energy released per unit area as the crack propagates; given by,

$$G_{1C} = \frac{K_{1C}^2(1-\nu^2)}{E} \quad (2)$$

where, ν = Poisson's ratio and E = Young's modulus of the material.

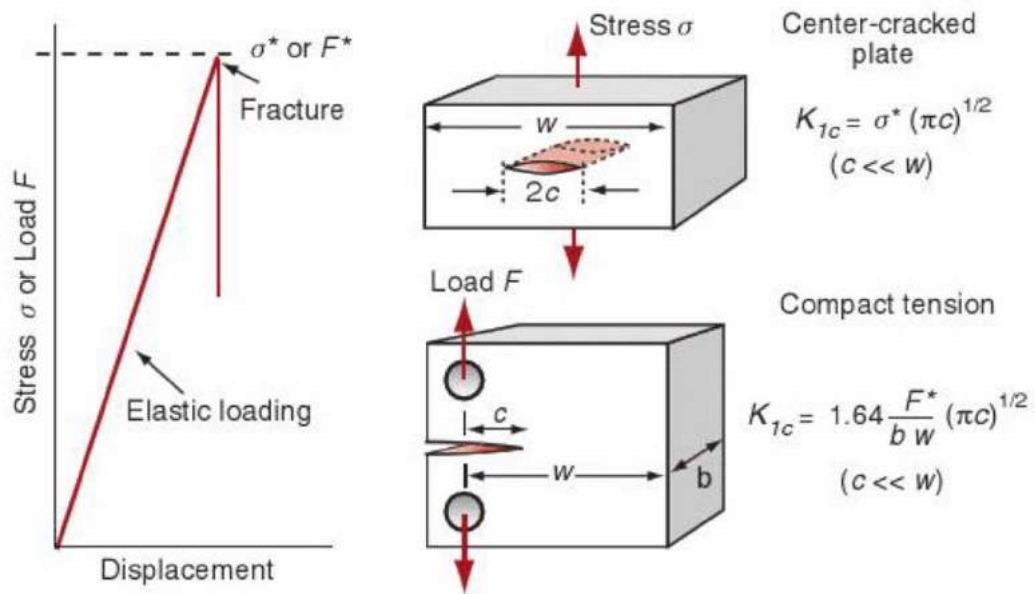


Figure 2.13. Measuring fracture toughness, K_{1C} .⁷⁵

2.6.4 Toughening Mechanisms

Several toughening mechanisms are reported for thermosetting polymers and their particulate filled composites. Secondary phase particles obstruct the

propagating crack which reduces the effective crack-driving force at the crack tip, stress intensity K . The reduction in stress intensity can be due to local changes in the microstructure, the mechanical properties, or environmental effects occurring in vicinity of the crack tip.⁷⁶ Some of common toughening mechanisms are, e.g. crack deflection, crack pinning, plastic deformation, microcracking and debonding and plastic void growth. Some of these mechanisms are discussed in the following sections.

Crack deflection

Crack deflection is a phenomenon where a propagating crack in a particle-matrix material will change its course when obstructed by a particle, which plays an important role in the toughening.⁷⁶⁻⁷⁷ When a crack advance towards a second phase particle, it will tilt at an angle of θ , out of its original plane and subsequent advance of the crack may result in crack front twist. The initial tilt angle depends on the orientation and position of the particle with respect to the propagating crack. The twisted and tilted cracks are subject to local stress loading. The tilted crack has opening (Mode I) and sliding (Mode II) contributions to the stress intensity while the twisted crack incorporates opening and tearing (Mode III) components. The overall enhancement in fracture toughness by crack deflection is sum of the local stress intensities arising from both tilted and twisted portions of crack.⁷⁸⁻⁷⁹ Therefore, the deflection process increases the total fracture surface area compared to the surface area generated by undeflected crack. The changes in fracture surface can be obtained by measuring the average surface roughness of a fracture surface using AFM topography data.⁷⁶ **Figure 2.14** illustrates the schematic of typical crack deflection process.

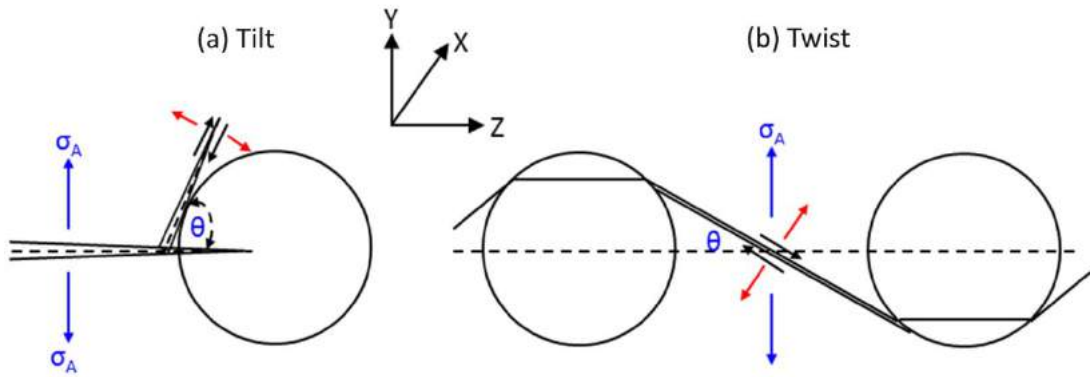


Figure 2.14. Schematic of typical crack deflection: (a) tilt, and (b) twist of the crack front.⁷⁸

Faber and Evans evaluated toughening mechanism of crack deflection processes in detail.⁷⁸ According to their evaluation; the increase of the toughness only depends on particle shape and the volume fraction of the second phase and not on particle size. The rod shape with high aspect ratio is the most effective morphology for deflecting propagating cracks and less effective morphologies are disc-shaped and spheres, respectively. Furthermore, fracture toughness is mostly determined by twist of crack front for rod-shaped and spherical morphologies whereas the initial tilt of a crack front plays the significant role in toughening for disc-shaped particles as shown in **Figure 2.15**.

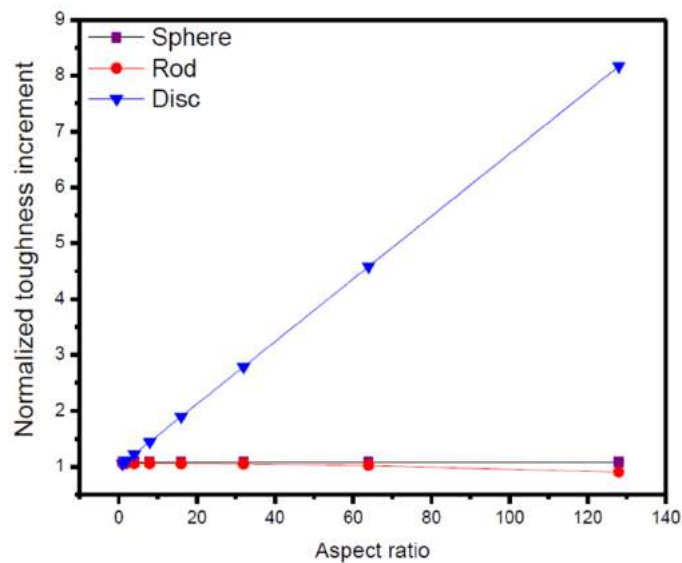


Figure 2.15. Normalized toughening increment for disc, spherical and rod shaped particles for initial crack tilt for volume fraction of 0.1.⁷⁹

Crack pinning

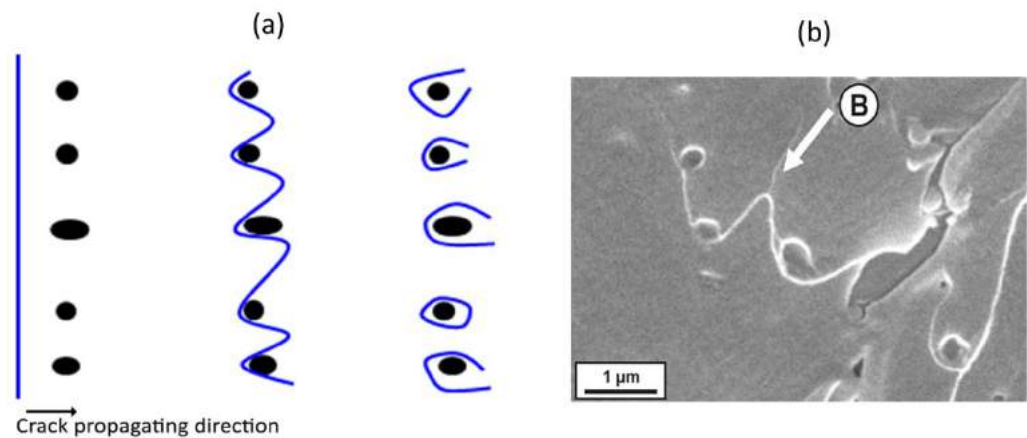


Figure 2.16. Schematic of crack pinning⁷⁹ and SEM image showing crack front bowing.⁷⁶

In this mechanism, rigid particles behave as impenetrable objects and the crack front between the particles moves on and extends by bowing out so that increases the crack length and hence consumes extra energy for crack propagation. The pinned cracks can create new surfaces and form ‘tails’ near the particles on the fracture surface which can be viewed by SEM.^{76, 80} A schematic of crack pinning process and SEM image of crack bowing is shown in **Figure 2.16**.

Debonding and plastic void growth

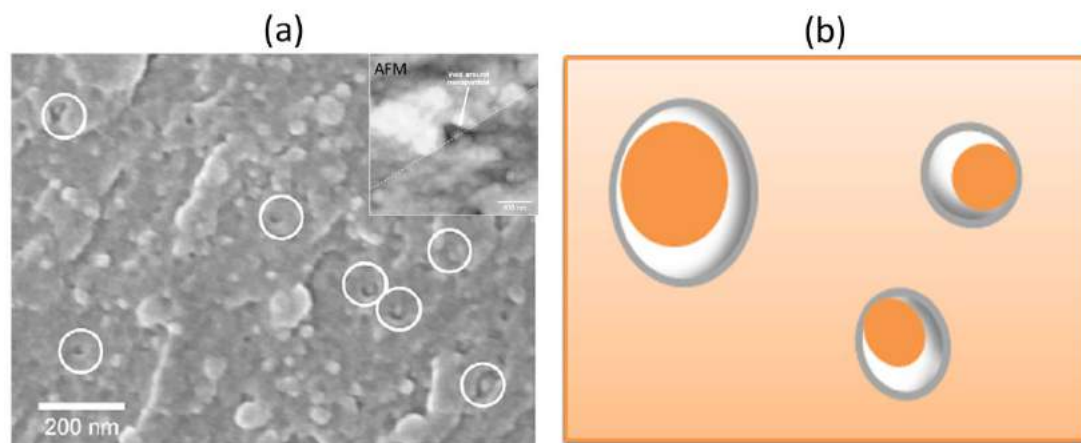


Figure 2.17. (a) SEM of the fracture surface of epoxy/nanosilica composite showing the voids around the nanoparticles⁸¹ (b) Schematic of particles debonded from matrix.⁷⁹

Debonding of micro or nanoparticles from the polymer matrix followed by plastic void growth has been shown as an important toughening mechanism in epoxy matrix composites. It is generally considered that debonding process absorbs little energy compared to the plastic deformation of the matrix. However, debonding reduces stress constraint at the crack tip and allows the matrix to deform plastically.^{79, 81} Johnsen et al. reported that the major toughening mechanism of nanosilica filled epoxy matrix was plastic void growth, evidenced by fracture surface observed by SEM and AFM (inset of (a)) as shown in **Figure 2.17(a)**.⁸¹ **Figure 2.17(b)** shows schematic of plastic debonded from matrix.

Crack bridging

Crack bridging is the most prominent toughening mechanism in fibre reinforced composites. In this process, rigid particles span the two crack surfaces and apply surface tractions that effectively reduce the applied stress at the crack tip. In addition, an alternative toughening mechanism proposed via crack bridging that the

energy consumed as rigid particles are plastically deformed and then torn. Physical evidence for the crack bridging mechanism can be examined by fracture surfaces using SEM where damaged particles on the plane of the crack can be seen.^{80, 82} In particular, improvements in toughness by crack bridging are influenced by size, stiffness and tear strength of particle. Increases in particle stiffness and tear strength result in an increase in crack shielding, hence toughness. Toughness should also be greater when larger particles are used.^{80, 82}

2.7 Epoxy Cure

2.7.1 Epoxy Resin

Epoxy resin was discovered in 1938, and epoxy resin has been used in a wide range of applications such as, paints, electricity, civil engineering etc. Epoxy resin has excellent mechanical properties, chemical resistance, electrical insulation and excellent bonding properties after curing. Furthermore, epoxy resin is able to have various different properties when it is cured with different curing agents.

Epoxy resin is a molecule containing more than one 1, 2-epoxy group. The basic structure of any epoxy resin has an aliphatic or aromatic polymer chain with at least two epoxide rings, generally located at each end of the molecule. The epoxy group is a cyclic ether group which is called a glycidyl group. The “idealized” structure of Diglycidyl ether of bisphenol A (DGEBA) is schematically shown in **Figure 2.18**.

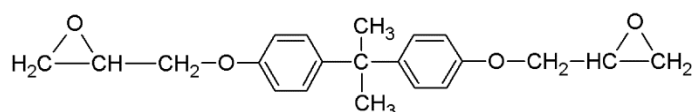


Figure 2.18. Schematic of epoxy resin, DGEBA.

2.7.2 Curing Agents

There are various kinds of functional groups containing molecules which are able to act as curing agents; these include amines, alcohols and anhydrides. The chemical nature of the curing agent/hardener controls the crosslink nature, and hence the cure kinetics and glass-transition temperature (T_g) of the epoxy. Some examples of curing agents are shown in **Figure 2.19**. The neat resin is generally mixed with a

curing agent in pre-determined ratios and heating is necessary to obtain the best polymer properties.

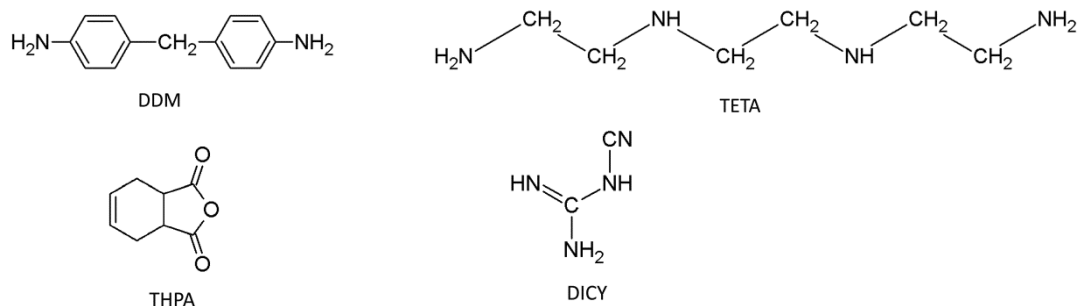
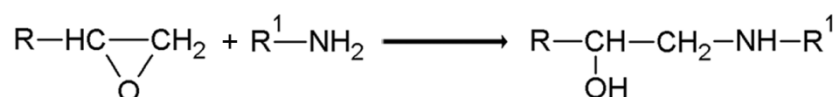


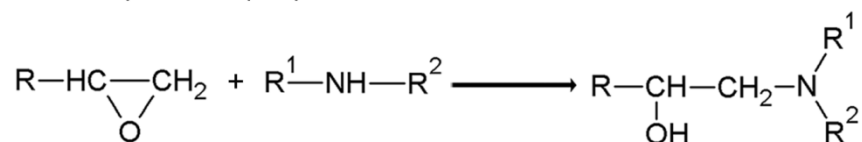
Figure 2.19. Structure of curing agents, Diaminodiphenylmethane(DDM), Triethylenetetramine(TETA), Tetrahydrophthalic anhydride (THPA), Dicyandiamine (DICY).

2.7.3 Cure Process

1. Primary amine-epoxy addition



2. Secondary amine-epoxy addition



3. Hydroxyl-epoxy addition (etherification)

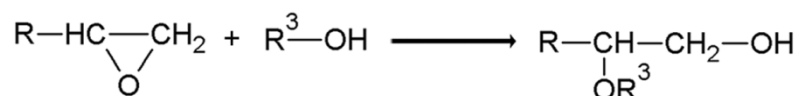


Figure 2.20. Major reactions in amine-cured epoxy resin.⁸³

It is vital to understand the mechanisms and the kinetics of the different reactions occurred during the epoxy cure since these parameters directly control the network structure and the properties of final cured resin. This work is concerned with amine curing reactions thus only these will be considered.

Epoxy resin reaction with amine generally involves three major reactions i.e; primary (1°) amine-epoxy, secondary (2°) amine-epoxy and hydroxyl-epoxy addition reactions as schematically shown in **Figure 2.20**. It has been reported that epoxide-

amine reaction requires some form of catalyst for reactions to proceed as acidity of amine itself is insufficient.⁸⁴⁻⁸⁵ Holubka et al. showed that proton donor additives such as water or hydrogen ion has a catalytic effect upon the rate of epoxide reaction.⁸⁴ The marked autocatalytic effect by the hydroxyl groups on amine-epoxy reaction (**Figure 2.20-1**) has been reported. Further, compounds that can increase the hydrogen ion activity had a catalytic effect on epoxy-amine reaction whereas solvents such as acetone, benzene etc. had a retarding effect.⁸⁵ Smith further studied the catalytic effect of hydroxyl on amine-epoxy reaction and proposed a hydrogen bonded complex between epoxy and hydroxyl groups which would react with an amine group as shown in Figure 21.⁸⁶ Similar to hydroxyl groups, amine group, for example, aniline, has been able to catalyse the amine-epoxy reaction via termolecular transition state as a mechanism similar to **Figure 2.21**.^{85, 87}

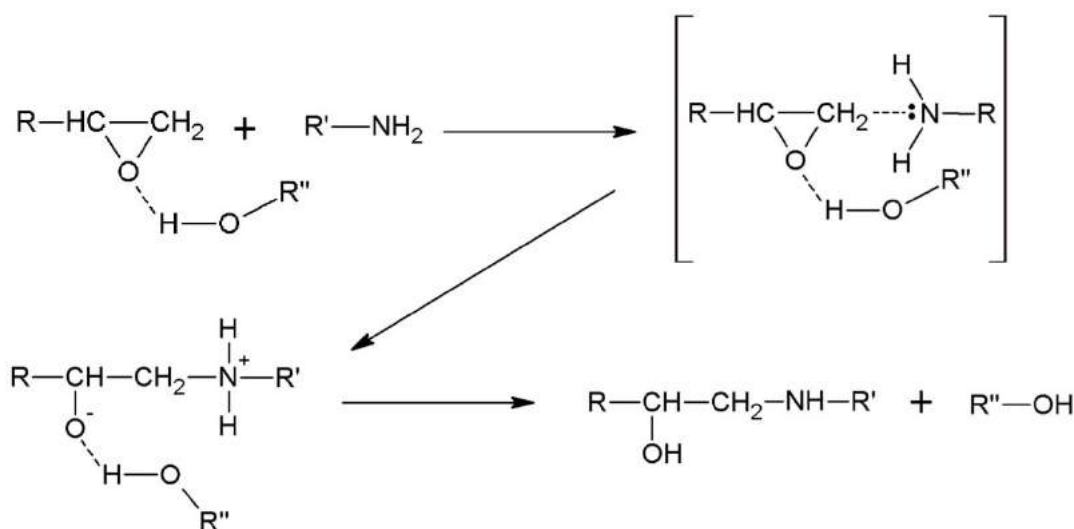


Figure 2.21. Mechanism for amine-epoxy reaction involving a termolecular transition state.⁸⁶

The secondary amine-epoxy reaction (**Figure 2.20-2**) occurs by the same mechanism as primary amine-epoxy reaction but at a lower reaction rate due to steric hindrance effect. The etherification reaction (**Figure 2.20-3**) is much slower than amine-epoxy reactions and the reaction has been found to be catalysed by the presence of tertiary amines or Lewis acids.^{85, 88}

2.7.4 Cure Monitoring Techniques

The amine curing processes and reaction mechanisms of several epoxy resin systems have been widely investigated by means of differential scanning calorimetry

(DSC) dynamic mechanical analysis (DMA) Raman spectroscopy, near-infrared (NIR) spectroscopy and infrared emission spectroscopy (IES). However, this work is concerned with DSC and IES thus only these will be discussed in detail in following sections.

Differential Scanning Calorimetry (DSC)

DSC is extremely sensitive to any reaction which involves heat flow changes thus any events that result in the release (exothermic) or absorption (endothermic) of energy can be studied using DSC.^{85, 89} It basically involves the measurement of the difference in energy required to keep a sample at a closely controlled temperature program compared to an inert reference. A curve of the heat flow required to keep the temperature of the two chambers the same is plotted against time or temperature. The area under the curve is directly proportional to the total energy. The cure kinetics and reaction mechanisms of epoxy systems have been studied extensively using DSC in both the isothermal and dynamic experiment methods.⁹⁰ The basic assumption made in DSC is that the heat evolution recorded by DSC is proportional to the extent of consumption of the functional groups ie; epoxy, amine.⁹⁰⁻⁹¹ From the isothermal experiment, the rate of reaction can be calculated using the equation 3 as shown below; if the energy changes in the system for full cure (H_{tot}) is known.

$$\frac{d\alpha}{dt} = \frac{1}{H_{tot}} \cdot \frac{dH}{dt} \quad (3)$$

$\frac{d\alpha}{dt}$ = rate of reaction; $\frac{dH}{dt}$ = rate of energy release versus time

The degree of cure or fractional conversion (α) can also be calculated at different time intervals, t by equation given below, using the total heat evolved in an isothermal cure experiment.

$$\alpha = 1 - \frac{\Delta H_t}{\Delta H_0} \quad (4)$$

Where; ΔH_0 is total heat of reaction for the system before curing and ΔH_t is the heat of reaction after cure for time t .

DSC is frequently used to determine other parameters such as activation energy and reaction order which are related to the network formation and processability of a material.⁹² DSC is also a useful tool to measure the T_g of a material. At low temperature, the heat flow remains relatively constant due to glassy nature of

polymer and heat flow starts increase at the point of T_g at which molecular motion occurs.⁹² The detail study of cure monitoring by DSC is described in Chapter 4 of this thesis.

Fourier Transform Infrared Emission Spectroscopy (FT-IES)

Infrared emission spectroscopy is a method in which sample is energized by heating and the emitted infrared light from the sample is measured to obtain a spectrum. Therefore, IES is unique and the method of measurement is entirely different from the transmission or reflection methods. In this method, external IR source is not required and sample itself act as light emitting source. Schematic diagram of IR emission spectrometer is shown in **Figure 2.22**.

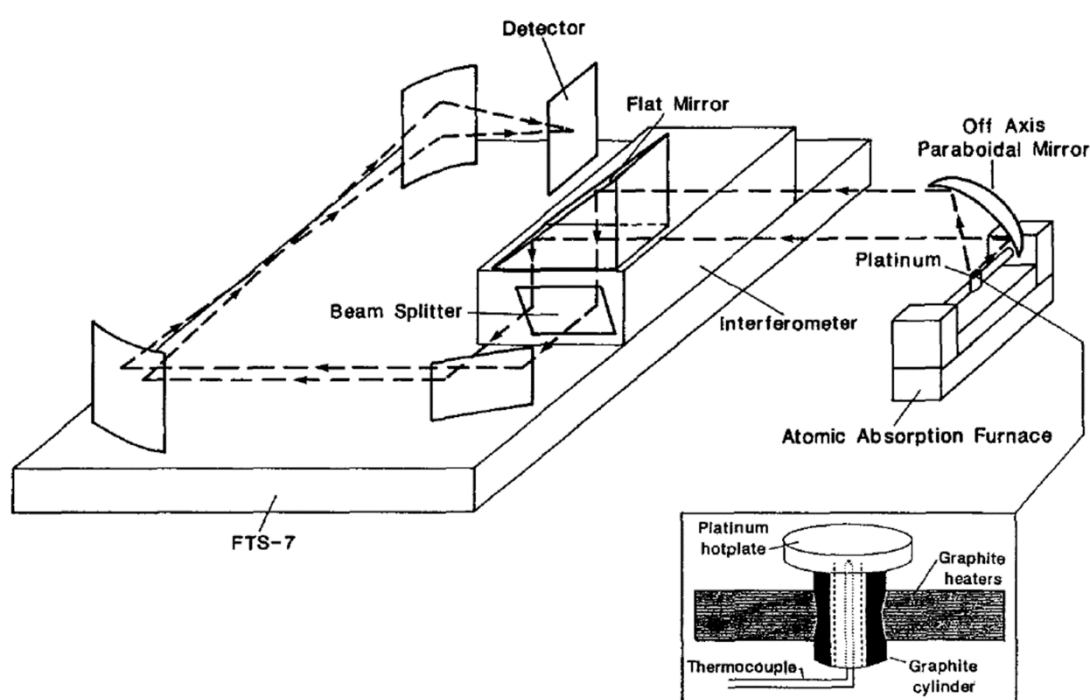


Figure 2.22. Schematic diagram of infrared emission spectrophotometer.⁹³

IR emission is isotropic and is hardly affected by the surface profile of base material and it also permits non-destructive and noncontact measurement of the sample.⁹⁴ Therefore, this method is applicable to powders, liquids, rough surfaces, or spherical objects etc. However, the thickness of the sample influences the spectrum. When a thick sample is heated, each layer emits characteristic emission. The layer emits most strongly where the absorptivity of the surface is greatest. The characteristic emission from layers well below the surface is absorbed by overlaying layers. This process called self-absorption and it is significantly noticeable when the

upper layers are cooler than that the layers well below the surface. When the thickness is increased, the effects of self-absorption may lead to loss of spectral information. Moreover, when the sample thickness is too high its transmittance will be zero at all wavelengths and will act the same as a black body. As it can be seen in the **Figure 2.23**, the emission spectrum from the thin layer has the appearance of a typical absorption spectrum of silicon grease while the spectrum of the thick layer looks more like a blackbody. When the sample is a thin film, reabsorption and temperature gradients are minimized and IR emission spectra equivalent to IR absorption may be obtained.⁹³

The dependence of the spectrum on the thickness of the sample has been well studied.⁹⁵⁻⁹⁶

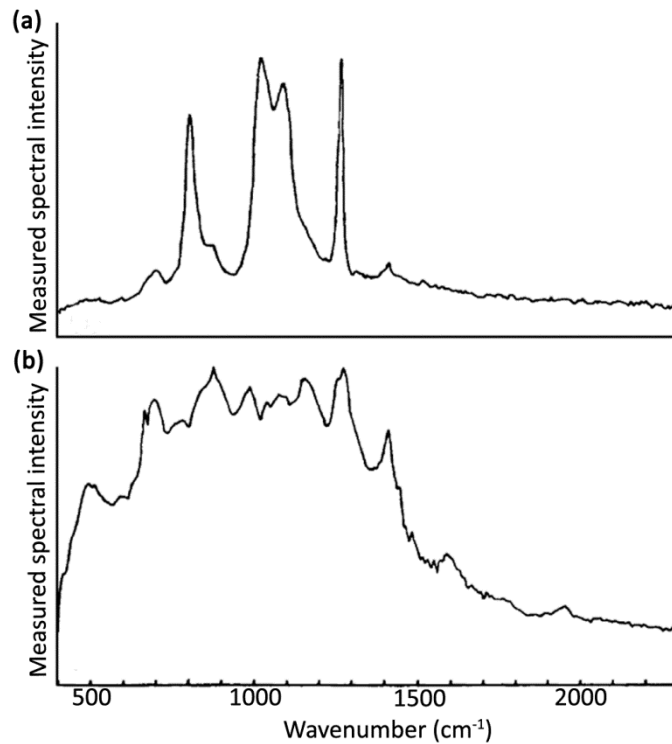


Figure 2.23. Single beam emission spectra of (a) a thin ($\sim 2\mu\text{m}$) layer, (b) thicker ($> 50\mu\text{m}$) layer of silicon grease.⁹⁷

The signal-beam emission spectra are obtained from the sample and the reference black body. The emission spectrum is obtained by ratioing the emission of sample to that of reference black body.

The emissivity, $\epsilon(\nu)$, of a sample at any wavenumber, (ν) is defined as the ratio of the energy emitted by a sample at a given temperature and the corresponding energy that would have been emitted by a blackbody source with the same geometry at the same temperature.^{93, 97}

$$\epsilon(\nu) = \frac{E_s(\nu, T)}{E_{bb}(\nu, T)} \quad (5)$$

where; E_s – energy emitted by the sample; E_{bb} – energy emitted by the blackbody

According to Kirchoff's law, for a material body in thermodynamic equilibrium, the absorbed and emitted energies are equal. A perfect black body absorbs all incident radiation so that it will also be the perfect emitter. Therefore, real sample always emits less energy than a blackbody.

Emission of infrared radiation occurs from all bodies at ambient temperature but emission intensity is weak at room temperature due to the low population of the higher vibrational states. At the cure temperatures of many resin-hardener systems ($\geq 100^\circ\text{C}$) there is a significant intensity in the “fingerprint” region of the IR spectrum so that the cure chemistry may be followed in real time. Applicability of the technique on very thin film samples gives an added advantage of offering the information on the interphase region where molecular chemical reactions occur during the curing process. Because of the specialized nature of the technique, limited investigation of amine curing of epoxy resin based on IR emission has been reported. Chapter 4 of this thesis will provide a comprehensive investigation of the effect of GO on epoxy curing process and its kinetics for the first time using IES technique.

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2.9 Recent Advances in Fabrication and Characterization of Graphene-Polymer Nanocomposites

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The authors listed below have certified that:

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Recent advances in fabrication and characterization of graphene-polymer nanocomposites

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Abstract

Graphene has attracted considerable interest over recent years due to its intrinsic mechanical, thermal and electrical properties. Incorporation of small quantity of graphene fillers into polymer can create novel nanocomposites with improved structural and functional properties. This review introduced the recent progress in fabrication, properties and potential applications of graphene-polymer composites. Recent research clearly confirmed that graphene-polymer nanocomposites are promising materials with applications ranging from transportation, biomedical systems, sensors, electrodes for solar cells and electromagnetic interference. In addition to graphene-polymer nanocomposites, this article also introduced the synergistic effects of hybrid graphene-carbon nanotubes (CNTs) on the properties of composites. Finally, some technical problems associated with the development of these nanocomposites are discussed.

Key words: Graphene, Polymer nanocomposites, Fabrications and Properties, Applications

2.9.2 Introduction

Development of novel polymer-nanocomposites (PNCs) has been attracting growing research effort worldwide over last few decades. In contrast to conventional composites, PNCs are featured by the fillers with a size of less than 100 nanometers. The advantage of polymer-nanocomposite is to provide value-added properties to the pristine polymer without sacrificing its processability, inherent mechanical properties and light weight.¹⁻² The key features in design and behaviour of PNCs include the size and property of nanofiller, and the interface between nanofiller and the matrix.³ In recent past, carbon nanotubes (CNTs) based PNCs have been widely investigated. The intrinsic bundling of CNTs, the limited availability of high quality nanotubes and high cost limited their applications.^{2, 4} Graphene has attracted attention as a promising candidate to create new PNCs due to its excellent properties and readily availability of its precursor, graphite. The incorporation of graphene can dramatically enhance the electrical, physical, mechanical, and barrier properties of polymer composites at extremely low loadings. The extent of the improvement is directly related to the degree of dispersion of the nanofillers in the polymer matrix.⁵

Graphene is a planar monolayer of sp^2 hybridized carbon atoms arranged into a two-dimensional (2D) honeycomb lattice with a carbon–carbon bond length of 0.142 nm. The adjacent graphene sheets in graphite are separated from each other by 0.335 nm, which is half the crystallographic spacing of hexagonal graphite. The adjacent graphene sheets are held together by weak van der Waals forces and thus the graphene sheets can slide with respect to each other giving graphite its soft and lubricating properties. Electrons in graphene behave like massless relativistic particles, which contribute to very peculiar properties such as an anomalous quantum Hall effect and the absence of localization.⁶ Graphene has demonstrated a variety of intriguing properties including high electron mobility at room temperature (250,000 cm^2/Vs) exceptional thermal conductivity ($5000\text{Wm}^{-1}\text{K}^{-1}$) and superior mechanical properties with Young's modulus of 1 TPa. Graphene can take part in certain classes of reactions including cyclo-additions, click reactions, and carbene insertion reactions.⁷ However, reactions on the surfaces of graphene hamper its planar structure. The destruction of the sp^2 structure leads to the formation of defects and loss of electrical conductivity.⁸

Graphene can be prepared by various methods including micromechanical cleavage, epitaxial growth, chemical vapour deposition (CVD), exfoliation of graphite intercalation compounds (GICs) and chemical oxidation-reduction methods.⁹⁻¹¹ Among these methods, micromechanical cleavage is more reliable and effective method to produce high quality graphene. However, this approach is limited by its low production yield.^{8, 12-13} Both epitaxial growth and CVD techniques can also produce high quality graphene with excellent physical properties. But, with these approaches, it is difficult to obtain a high yield to satisfy the need as composite fillers. GICs are formed by the insertion of atomic or molecular layers of different chemical species between the layers of graphite. Exfoliation of GICs can produce large quantity of graphene with perfect graphene structure. However, graphene obtained from this method consists of multilayered sheets because of restacking of graphene layers after deintercalation. At present, the most viable route to produce graphene in considerable quantities is reduction of graphite oxide. Graphite oxide is generally synthesized through oxidation of graphite using strong mineral acids and oxidizing agents, typically via treatment with KMnO_4 and H_2SO_4 based on Hummers method.¹⁴ Compared to pristine graphene, graphene oxide (GO) is heavily

oxygenated and its basal plane carbon atoms are decorated with epoxide and hydroxyl groups and its edge atoms with carbonyl and carboxyl groups. Hence, GO is highly hydrophilic and the presence of these functional groups reduces interplanar forces, which can improve the interfacial interaction between GO and some polymers and thus the dispersion state of GO in polymer matrices.^{13, 15} But, the oxidizing chemical treatment inevitably generates structural defects such as Stone–Wales (S–W) type defects, single and multiply vacancies, dislocation like defects, carbon adatoms, or accessory chemical groups. These atomic scale structural defects adversely affect the mechanical performance of graphene.¹⁶⁻¹⁷ Further, the structural defects interrupt the electronic structure of graphene and change it to semi-conductive.^{8, 12, 18-19} High temperature thermal annealing or low temperature chemical reduction processes can be carried out to make insulating GO to conductive graphene. Thermally reducing process is generally carried out by rapid heating (2000°C/min) up to 1050°C in vacuum or inert atmosphere while chemical reduction is based on chemical reactions of GO with chemical reducing agents.^{13, 20} Most commonly used chemical reducing agents are hydrazine and its derivatives²¹⁻²², metal hydrides²³⁻²⁴, HI acid²⁵, hydroquinone²⁶, p-phenylene diamine²⁷ etc. Different reducing processes result in different electrical properties of reduced graphene oxide (RGO). For example, Shin et al.²⁴ have found that the sheet resistance of graphite oxide film reduced using NaBH₄ is much lower than that of films reduced using hydrazine. Generally, thermally reduced GO exhibits a higher conductivity compared to chemically reduced GO as seen in **Figure 2.24**.²⁸ More details of preparation methods and properties of graphene and its derivatives can be found in elsewhere.^{5, 8, 12, 20, 29}

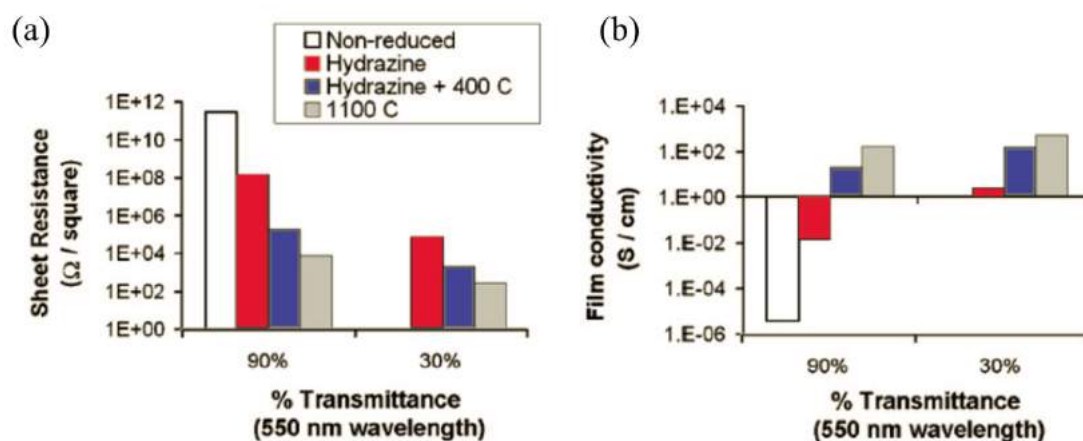


Figure 2.24. Comparison of the electrical properties of GO films of different optical transparency after undergoing different reduction treatment. (a) Measured sheet resistance of the films (b) Film conductivity calculated from the sheet resistance and film thickness. Thickness of the films in the 90% transmittance group is 8.5, 5.0, 2.9 and 8.1nm from left to right. The corresponding thickness averages are 55.3, 30.9, 66.9 nm for the films in the 30% transmittance group.²⁸

2.9.3 Graphene-polymer nanocomposites

Graphene and its derivatives filled polymer nanocomposites have shown immense potential applications in the fields of electronics, aerospace, automobile, defence industries, green energy, etc due to its exceptional reinforcement in composites. To take full advantage of its properties for applications, integration of individual graphene in polymer matrices is prime important. Compared with CNTs, graphene has a higher surface-to-volume ratio, makes graphene potentially more favourable for improving the properties of polymer matrices, such as mechanical, electrical, thermal, and microwave absorption properties. More importantly, graphene is much cheaper than CNTs, as it can be easily derived from a graphite precursor in large quantity. Many factors, including the type of graphene used and its intrinsic properties, the dispersion state of graphene in the polymer matrix and its interfacial interaction, the amount of wrinkling in the graphene, and its network structure in the matrix can affect the final properties and applications of graphene/polymer nanocomposites.¹⁹

2.9.3.1 *Synthesis of graphene-polymer nanocomposites*

Graphene-polymer nanocomposites have been prepared using three synthesis routes 1. Solution mixing 2. Melt blending and 3. *In situ* polymerization, which are most common synthesis strategies of the polymer matrix composites.

Solution mixing

Solution mixing is the most straightforward method for preparation of polymer composites. The method consists three steps; dispersion of filler in a suitable solvent by, for example, ultrasonication, incorporation of the polymer and removal of the solvent by distillation or evaporation.^{2, 29} During the solution mixing process, polymer coats graphene sheets and when the solvent is evaporated, the graphene sheets reassemble, sandwiching the polymer to form the nanocomposite.⁵ The solvent compatibility of the polymer and the filler plays a critical role in achieving good dispersion. This strategy can be employed to synthesize polymer composites with a range of polymers such as Poly (vinyl alcohol) (PVA)³⁰⁻³², Polyvinyl fluoride (PVF)³³, Polyethylene (PE)³⁴⁻³⁵, Poly(methylmethacrylate) (PMMA)³⁶, Poly(ethylmethacrylates)(PEMA)³⁷, Polyurethane (PU)³⁸. However, solvent removal is a critical issue. Due to the oxygen functional groups, GO can be directly mixed with water soluble polymers such as PVA. Zhao et al.³⁰ have prepared GO-PVA composites by directly adding of PVA powder into the exfoliated aqueous dispersion of GO at 85°C and stirring for 6h. Field Emission Scanning Electron Microscopy (FESEM) images reveal that most of the GO sheets are fully exfoliated and clearly well-dispersed in the PVA matrix, while there are few restacks together. XRD observations of composites also confirmed the molecular level dispersion of GO in PVA matrix. Chemical functionalization can improve the solubility and interaction of GO with polymers. Various types of polar polymers such as PMMA, PAA, PAN and PS have been successfully mixed with functionalized GO (f-GO) for example, GO functionalized with isocyanate, amine^{35, 39} or polymer grafted GO⁴⁰ using solution mixing technique. Functionalization of graphene sheets both beneficial to disperse in water and organic solvents with reduced agglomeration and to obtain higher loading of graphene in the composites. Ultrasonication may help to obtain a homogenize dispersion of graphene sheets; however, long time exposure to high power sonication can induce defects in graphene which are detrimental to the composite properties.⁸ Oxygen containing functional groups on the GO can break the conjugated structure

and localize p-electrons, leading to decrease of both carrier mobility and carrier concentration. In addition, the attached groups modify the electronic structure of graphene and serve as strong scattering centers that affect the electrical transport. As a result, GO sheets are typically insulating, exhibiting a sheet resistance of about 10^{12} Ω/sq or higher.⁴¹ Reduction of GO can recover the conjugated network of graphene sheets, resulting in recovery of its electrical conductivity and other properties. Conversely, reduced graphene oxide will result in irreversible restacking, which then makes dispersion of individual sheets in a polymer matrix intricate. *In situ* reduction can be used to both restore the conductivity and prevent restacking because of the presence of polymers in the solution mixture during the reduction.¹⁹ Traina and co-workers⁴² have prepared *in situ* chemically reduced GO in polyvinyl alcohol (PVOH) matrix using hydrazine hydrate in mild thermal condition. The chemically reduced GO/PVOH composite exhibits the surface electrical resistivity of 3.1×10^5 Ω/sq at filler loading of 9.4 wt% i.e. about one order of magnitude lower than the value obtained for PVOH-GO composites at the same filler content. Dramatic enhancement of electrical conductivity for the *in situ* reduced GO-Nafion nanocomposites by exposure to hydrazine has been reported by Ansari et al.⁴³ The graphene-Nafion nanocomposites containing 5 wt% GO exhibits the electrical conductivity of 1.3 Sm^{-1} while the corresponding unreduced nanocomposites show much lower conductivity of $4 \times 10^{-2} \text{ Sm}^{-1}$. Dramatic enhancement of electrical conductivity indicated sufficient accessibility of the inorganic GO nanosheets to the reducing agent, through the nanochannels formed by the polymeric ionic domains. The chemically reducing process has been successfully used to fabricate other polymers such as vinyl acetate/vinyl chloride co-polymers.⁴⁴ However, suitable reducing agents are needed to be selected depending on the type of polymer as *in situ* reduction may cause polymer degradation.¹⁹ The *in situ* thermally reducing of GO have not been successful since the majority of polymers cannot stand high temperature that is necessary for the reduction.

Melt blending

Melt blending is a more practical and versatile technique especially for thermoplastic polymers. The technique employs a high temperature and shear force to disperse fillers in the polymer matrix. High temperature softens the polymer matrix allowing easy dispersion of reinforcement phase. This process is free from toxic solvent but less effective in dispersing graphene in the polymer matrix

especially at higher filler loadings due to increased viscosity of the composites.⁸ Another drawback of this technique is buckling, rolling or even shortening of graphene sheets during mixing due to strong shear forces resulting in reducing its aspect ratios which is not favourable for better dispersion.¹⁹ Kim et al.³⁵ have investigated the effect of blending methods on properties of graphene/polyethylene nanocomposites. Unlikely fully isolated, single graphene sheets blended in solution, melt blended samples appear predominantly phase separated and complete exfoliation is rarely observed (**Figure 2.25**). They have also found that, melt blended composites did not display notably improved electrical conductivity nearly up to 1.2 vol% graphene loading whereas solvent blended graphene could reduce the surface resistance of polymer at even as low as 0.2 vol%. However, regardless of blending methods, tensile modulus increased with incorporation of graphene into PE matrix. Similar studies and findings have been reported for graphene/polyurethane nanocomposites by Kim and co-workers in reference.³⁸ However, in contrast, Bao et al.⁴⁵ have successfully prepared graphene/ poly (lactic acid) (PLA) nanocomposites by melt blending with improved properties. They have adopted a master-batch strategy to disperse graphene into PLA by melt blending. The graphene was well dispersed and the obtained nanocomposites present markedly improved crystallinity, rate of crystallization, mechanical properties, electrical conductivity and fire resistance. The properties are dependent on the dispersion and loading of graphene, showing percolation threshold at 0.08 wt%. A range of composites, such as Poly (vinylidene fluoride) (PVDF)⁴⁶, Polystyrene (PS)⁴⁷, polypropylene (PP)⁴⁸⁻⁴⁹ have been prepared using this technique.

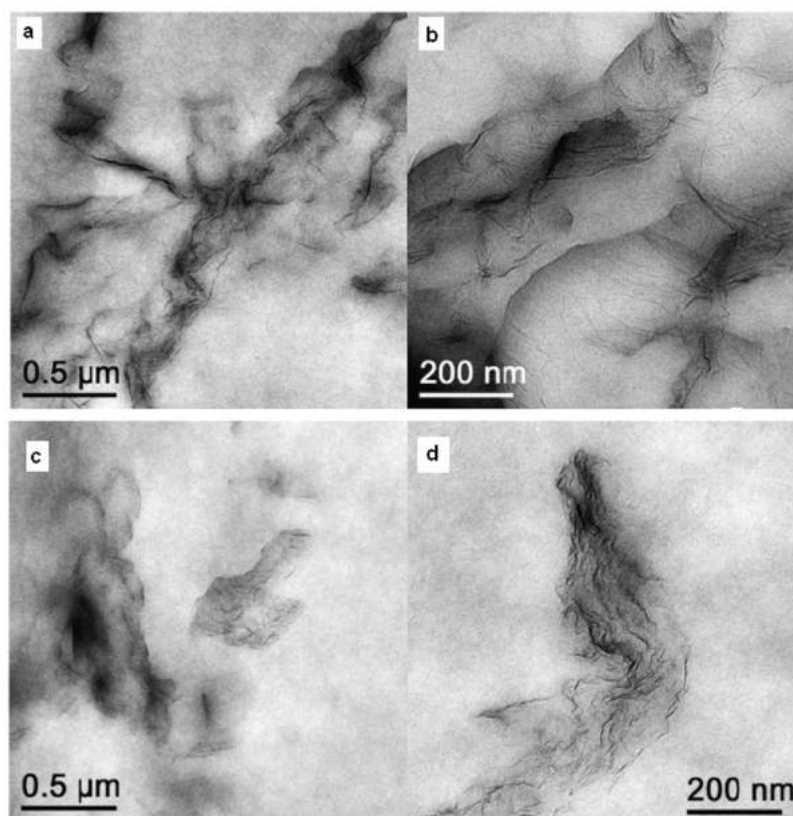


Figure 2.25. TEM images of 1wt% Thermally reduced Graphene (TRG) /PE prepared by (a,b) solvent mixing (c,d) melt blending.³⁵

In situ polymerization

In situ polymerization is another often used technique to fabrication graphene polymer nanocomposites such as epoxy⁵⁰⁻⁵³, PMMA⁵⁴, Nylon 6⁵⁵, PU⁵⁶, poly (butylene terephthalate) (PBT)⁵⁷, polyaniline (PANI)⁵⁸, PE⁵⁹ etc. In this method, graphene or its derivative is first swollen in the liquid monomer, and then appropriate initiator is dispersed. Polymerization is initiated either by heat or radiation. The intercalation of monomers into the layered structure of graphite, during *in situ* polymerization, increases interlayer spacing and exfoliates graphene platelets producing well-dispersed graphene in polymer matrix after polymerization. *In situ* polymerization technique makes possible the covalent bonding between the functionalized sheets and polymer matrix via various chemical reactions. Major drawback of this technique is the increase of viscosity with the progress of polymerization process that hinders manipulation and limits load fraction.^{2, 19} Besides, in some cases, the process is carried out in the presence of solvents, thus solvent removal is a critical issue similarly in the solvent mixing technique.¹⁹ Zaman

et al.⁵¹ have achieved the lowest electrical conductivity percolation threshold for epoxy reported, by adopting in situ polymerization technique in preparing chemically modified graphene/epoxy composites. Their investigation showed a general approach to make highly dispersed graphene/polymer nanocomposites with good control over the structure and the properties as shown in **Table 2.2** and **Figure 2.26**.

Table 2.2. Properties of pristine epoxy and its graphene nanocomposites. Reprinted with the permission from reference.⁵¹

Materials	Young's modulus [GPa]	Tensile strength [MPa]	Elongation at break [%]	Plane-strain fracture toughness, K_{IC} [MPa m ^{1/2}]	Critical strain energy release rate G_{IC} [kJm ⁻¹]	Glass transition temperature T_g [°C]
Neat epoxy	2.692±0.129	63.982±2.14	5.31±0.29	0.657±0.034	140.7±7.9	83.4
0.122 vol% epoxy/graphene	2.992±0.234	61.51±1.49	4.01±0.19	1.004±0.033	295.6±4.1	92.3
0.244 vol% epoxy/graphene	3.158±0.089	51.44±0.12	3.50±0.11	1.258±0.030	439.7±8.8	90.0
0.439 vol% epoxy/graphene	3.412±0.173	49.21±2.94	2.68±0.44	1.472±0.023	557.3±2.7	95.6

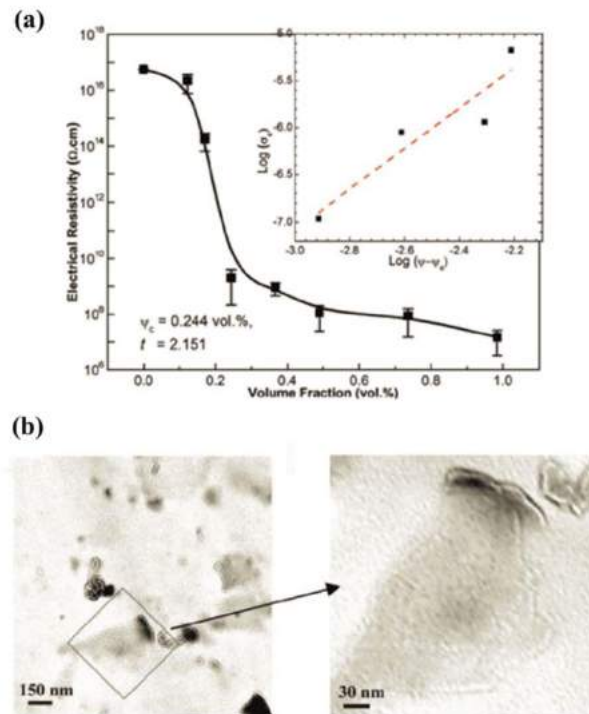


Figure 2.26. (a) Electrical resistivity of epoxy and its graphene nanocomposites (b) TEM images of graphene/epoxy nanocomposites.⁵¹

2.9.3.2 Properties of Graphene-Polymer Nanocomposites

Mechanical properties

Experimental discovery of graphene as a nanomaterial with its intrinsic strength (~ 1.0 TPa) and elastic modulus (125 GPa), has opened a new and interesting area in material science in recent years. In fact, better understanding of chemistry and intrinsic properties of graphene with different approaches of making it has led scientists to design graphene filled polymer composites with enhanced mechanical, thermal, electrical and barrier properties. Similar to other composites, the extent of the improvement is related to many factors such as the reinforcement phase concentration and the distribution in the host matrix, interface bonding and the reinforcement phase aspect ratio. The most important aspect of these nanocomposites is that all the property enhancements are obtained at a very low filler loading in the polymer matrix.²⁹ **Table 2.3** lists the percentage enhancement in the mechanical characteristics of graphene based polymer nanocomposites with respect to the base polymer matrix.

It can be observed from the table that the addition of graphene to polymer matrices can significantly influence their mechanical properties. However, the degrees of improvement are different. For an example, the tensile strength increase varies from ~ 0.9 for graphene/epoxy at 1.0 wt%⁶⁰, 77 for CRGO/PE at 3.0 wt%⁶¹ and 150 for functionalized CRGO/PVA at 3.0 wt%³⁰. This variation is mostly due to the structure and intrinsic properties of graphene, its surface modifications, the polymer matrix and also different polymerizing processes.¹³ Although, the pristine graphene has the highest theoretical strength, it has shown poor dispersion in polymer matrices due to restacking as well as its low wettability, resulting in decreased mechanical properties of reinforced nanocomposites. GO is commonly used to improve the mechanical properties of graphene/polymer composites, for the reasons of excellent mechanical properties (eg: Young's modulus of GO monolayer is 207.6 ± 23.4 GPa⁶²), abundant functional groups, which facilitate strong interfacial interaction and load transfer from the host polymers to the GO and ability to significantly alter the van der Waals interactions between the GO sheets, making them easier to disperse in polymer matrices.⁶³

Table 2.3. Mechanical properties of graphene-polymer nanocomposites.

Matrix	Filler	Filler loading (wt% ^a , vol% ^b)	Fabrication process	% increase compared to neat polymer				Reference
				Tensile strength	Elastic modulus	Fracture energy (G _{1c})	Fracture toughness (K _{1c})	
Epoxy	f-GP ¹	0.489 ^b	<i>In situ</i>	~22.6	~26.7	~296	~55.3	53
	f-GP ¹	1.5 ^a	<i>In situ</i>		~7.7		~55	52
	TRGO ²	0.1 ^a	<i>In situ</i>	20			25	64
	f-GP ¹	4.0 ^a	<i>In situ</i>	-15	21.6	200	100	65
	GP ³			-23	7.4	104.3	50	
	TRGO ²	0.1 ^a	<i>In situ</i>	40	31	126	53	66
	f-GP ¹	1.0 ^a	<i>In situ</i>	30	50		Negligible	67
	TRGO ²	0.125 ^a	<i>In situ</i>	~45	~50	115	65	65
	GNR ⁴	0.3 ^a	<i>In situ</i>	22	30		Marginally increased	68
	GO	0.1 ^a	<i>In situ</i>	12	~4	29	28	69
	GP ³	1.0 ^a	<i>In situ</i>	0.9	22.6			60
	GO	1.0 ^a	Solution blending	~0.5	~3.6			34
	TRGO ²	1.0 ^a	Solution blending		-8.9			36
	CRGO ⁵	3.0 ^a	Melt blending	77	87			61
PU	f-GP ¹	0.5 ^a	Melt blend.		~49.1			38
			Sol.blend.		~98.4			
			<i>In situ</i>		~14.7			
PVA	CRGO ⁵	1.8 ^b	Solution blending	150	~940			30
	f-CRGO ⁶	3.0 ^a	Solution blending	177	86		235	31
PVAc	GO	0.07 ^a	Solution blending	~38.7	~9.35			70
	f-GO ⁷			~55.30	~11.7			
PP	CRGO ⁵	1.0	Melt blending	75	74			48
PMMA	GO	2.0 ^a	<i>In situ</i>	15.0	29.9			54
	CRGO ⁵			-1.9	35.8			

¹ Functionalized graphene, ² Thermally reduced GO, ³ Graphene, ⁴ Graphene nanoribbons, ⁵ Chemically reduced GO, ⁶ Functionalized CRGO, ⁷ Functionalized GO

El Achaby et al.⁷¹ have fabricated graphene oxide nanosheets (GOn)/PVDF nanocomposite films by solution casting method with various GOn contents in dimethylformamide (DMF). Due to the strong and specific interaction between carbonyl group (C=O) in GOn surface and fluorine group (CF₂) in PVDF, the GOn

were homogeneously dispersed and distributed within the matrix. As shown in **Figure 2.27**, the Young's modulus and tensile strength of PVDF were increased by 192% and 92%, respectively with the addition of 2 wt. % GOn. The morphology of nanocomposites (**Figure 2.28**) where the majority of GOn has been exfoliated and uniformly dispersed throughout the polymer matrix with almost no large agglomeration is in excellent agreement with observation of improved mechanical properties. The property enhancements can be related to the strong and specific interfacial interaction that results in the adsorption of macromolecular chains of PVDF on to the GOn surface.

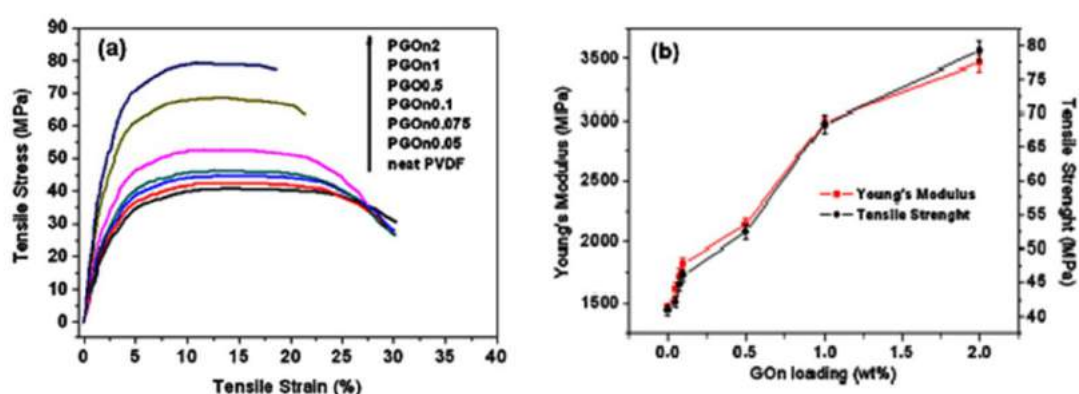


Figure 2.27. (a) Typical stress-strain curves of PVDF/GOn (b) Young's modulus and tensile strength versus GOn contents.⁷¹

Strong interfacial adhesion between the graphene platelets and polymer matrix is crucial for effective reinforcement. Incompatibility between phases may lower stress transfer due to poor interfacial adhesion, resulting in a lower composite strength properties. Covalent or non-covalent functionalization of graphene based materials can be used to tailor the interface to promote stronger non-covalent interaction between the matrix and graphene platelets. Hydrogen bond interactions and Van der Waals interactions were reported as the responsible interactions for improved mechanical properties.^{32, 72-73}

Although physical interactions can improve the properties of composites, the relative movements between the filler and matrix cannot be avoided under external stresses, which limit the attainable maximum strength. In order to alleviate this problem, chemical tailoring of the interface between filler and matrix is important which may provide the most effective means to increase the interfacial shear strength for improving stress transfer due to formation of covalent bonds between the filler

and matrix.²⁹ For example, GO was covalently bonded to PU via the formation of urethane bonds (-NH-CO) from the reaction between the hydroxyl groups (-OH) on the surface of the GO and -NCO groups on the ends of PU chains as shown in **Figure 2.29**. This chemical bonding has led to the increase in toughness by 50% at 1 wt% loading without losing its elasticity.⁷⁴ Various chemical modifications have been reported in literature.^{31, 47, 75-78}

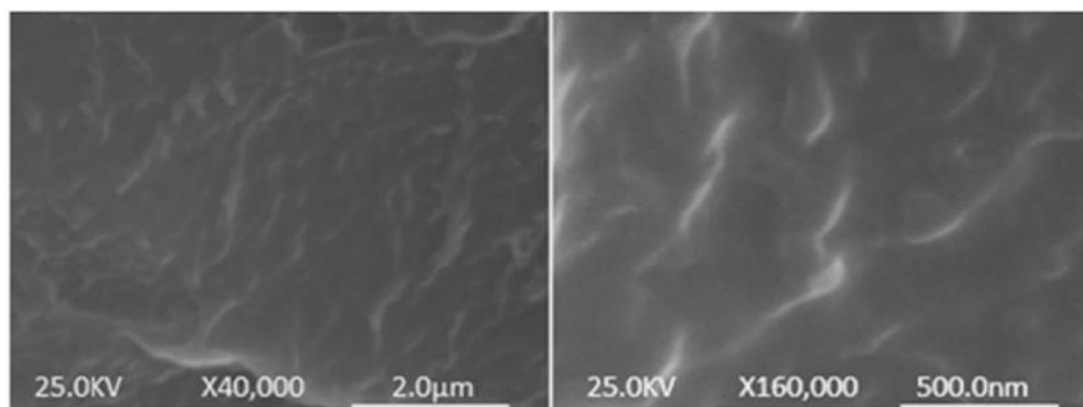


Figure 2.28. Low (left) and high (right) magnification SEM of PVDF/GON nanocomposite films at 2 wt% GON.⁷¹

Other than the intrinsic properties and interfacial interaction between the graphene and host polymer, a wrinkled topology of graphene would produce an enhanced mechanical interlocking and adhesion with the polymer chains and consequently strengthens the interaction and load transfer between graphene and the polymer matrix.^{2, 13, 73, 79} Comparison of micro-mechanical predictions, utilizing Halpin-Tsai model, with experimental data shows that the theoretically predicted value for Young's modulus of the graphene/epoxy nanocomposites is ~13% lower than the experimental results. However, the predictions for CNTs/epoxy composites are over predicted the test data by up to 12%.⁶⁶ It has been suggested that the wrinkled structure of graphene, which is different from the rectangular shape assumed by the model, may play a significant role in reinforcement. Recently, molecular dynamics and molecular mechanics simulation studies⁸⁰ showed that besides the interfacial bonding energy, the mechanical interlocking plays important roles in the interfacial bonding characteristics between the graphene and polymer matrix. The study suggested nanoscale surface roughness of graphene, arise due to absorption of chemical functional groups, can more strongly interlock with the polymer molecules to arrest the polymer chains slippage and facilitate better load

transfer stronger. Rafiee et al.⁶³ have reported significant reinforcement from TRGO, attributed to strong interfacial bonding augmented by mechanical interlocking with matrix due to the nanoscale roughness of the platelets.

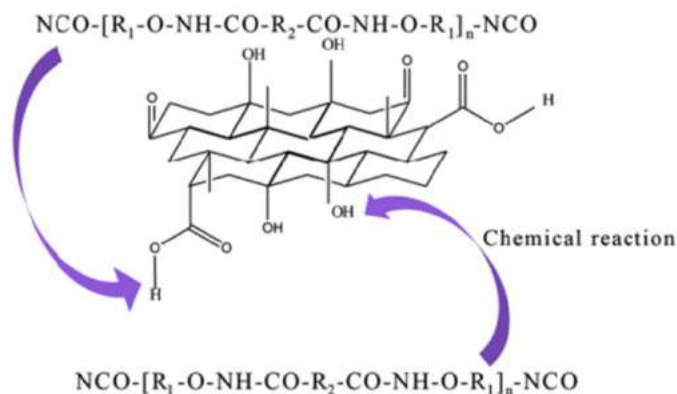


Figure 2.29. The schematic illustration for the formation of the covalent bonds between the GO and PU matrix.⁷⁴

Beyond the mechanical reinforcement, other improvements in fatigue^{63, 81-82}, creep⁸³, crazing⁸², fracture toughness^{63, 66, 69}, impact strength⁸⁴, of the graphene-polymer nanocomposites have been reported. The smaller creep strain was shown in epoxy nanocomposites with 0.1wt% graphene at the higher stress loading of 40 MPa than that of pristine epoxy.⁸³ This reflects the less deformation of nanocomposites compared to pristine epoxy. Further, it was found that the strain at the end of the hold period (after 36h) was 15% smaller in the composite compared to pristine epoxy. Conversely, the creep behaviour is essentially identical for the filled and pristine epoxy at the smaller stress load of 20 MPa. Addition of 0.125wt% TRGO into epoxy improved the fracture toughness of nanocomposite by ~65% compared to pristine epoxy.⁶³ It is worthy to note that to achieve comparable increase (~62%) in K_{IC} , the required weight fraction (~14.8%) of SiO_2 nanoparticles is ~120 fold larger than TRGO. Similarly, to obtain a 65% increase in K_{IC} , the volume fraction of Al_2O_3 (~5%) and TiO_2 (~10%) nanoparticles in epoxy is ~30 to ~60 fold larger than TRGO. For CNTs-epoxy composites, the best reported enhancement in K_{IC} is ~43% which occurs at 4-fold higher nanofiller weight fraction.⁶⁶ However, for higher filler loading of TRGO, the enhancement in K_{IC} diminishes and finally begins to approach the pristine epoxy value as shown in **Figure 2.30 (a)**. This indicates that dispersion of higher fraction of two dimensional graphene in polymer matrix is more

challenging. It has also shown significant reduction in crack growth rate for the nanocomposite compared to the pristine epoxy as illustrated in **Figure 2.30 (b)**.

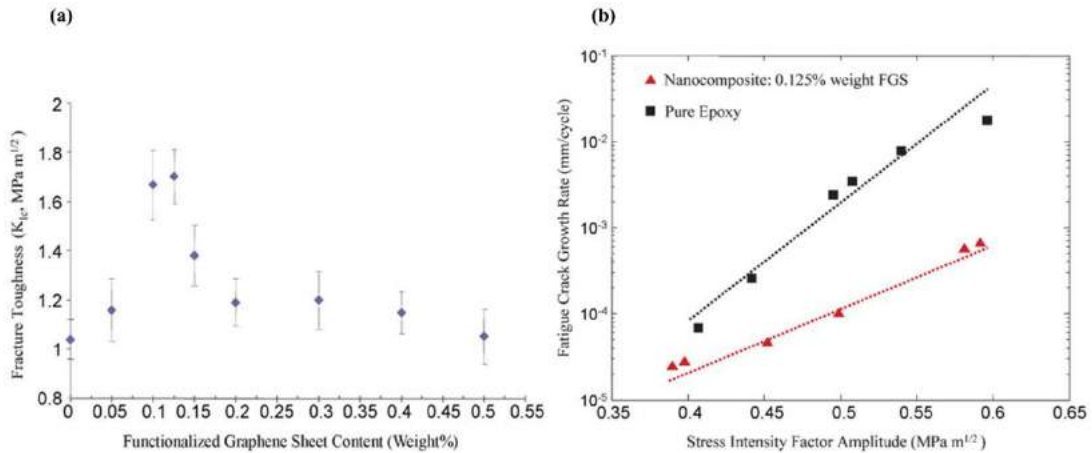


Figure 2.30. (a) Mode I fracture toughness (K_{IC}) plotted as a function of the weight fraction in the epoxy matrix. (b) Crack growth rate (da/dN) plotted as a function of the stress intensity factor amplitude (ΔK) for the pristine epoxy and nanocomposite with 0.125 wt% of TRGO.⁶³

Conductive properties

In **Table 2.4**, we summarize the electrical and thermal conductive properties of graphene-polymer nanocomposites from the literature with respect to base polymer matrix.

Electrical conductivity

The most fascinating property of graphene is its very high electrical conductivity. When used as fillers with insulating polymer matrix, conductive graphene may greatly enhance the electrical conductivity of the composites. The filled composite materials exhibit a non-linear increase of the electrical conductivity as a function of the filler concentration. At certain loading fraction, known as percolation threshold, the fillers are able to form a network leading to a sudden rise of the electrical conductivity of the composite.² Various factors influence the electrical conductivity and the percolation threshold of the composites such as concentration of filler, aggregation of filler, processing methods, the presence of functional groups and aspect ratio of graphene sheets, inter-sheet junction, distribution in the matrix, wrinkles and folds etc.^{2, 8} The filler need not be in direct contact for current flow, rather conduction can take place via tunnelling between thin polymer layers surrounding the filler particles, and this tunnelling resistance said to

be the limiting factor in the composite conductivity.⁸⁵ The pristine graphene has the highest conductivity; however difficulty in producing a large amount by mechanical exfoliation limits its use. Reduction of electrically insulating graphene oxide eliminates the oxygen functional groups and partially restores the electrical conductivity, making reduced graphene oxide suitable conductive filler for composite. It is reported that thermally reduced GO has higher electrical conductivity than chemically reduced GO due to the absence of oxygenated functional groups.⁸ Kim et al.³⁸ have studied the effect of thermal and chemical reduction of GO on electrical properties of graphene/ PU composites. The lower percolation threshold of <0.5 vol% was reported for TRGO while >2.7 vol% for graphite. However, CRGO and GO did not show decrease in surface resistance due to loss of electrical conductivity after graphite oxidation. On the contrary, recent work by Shen et al.⁸⁶ have revealed that electrical conductivity of CRGO (2.5×10^3 S/m) (chemical reduction using glucose) is higher by four orders of magnitude compared to conductivity of TRGO (2.8×10^{-1} S/m), much higher than that of GO (2.7×10^{-7} S/m). It has been suggested that lower conductivity of TRGO is possibly due to the presence of oxygenated species and the smaller sp^2 domains created by thermal reduction of GO which makes it difficult to restore the conductivity network in reduced graphene. They have also observed that significantly high electrical conductivity value for Polylactic acid (PLA)/rGO-g compared to PLA/GO nanocomposites. For example, at 1.25 vol. %, PLA/GO has a conductivity value of 6.47×10^{-13} S/m, while the value of PLA/rGO-g is 2.2 S/m.

Interestingly, recent work on Zhang and co-workers³⁶ studied the effect of surface chemistry of graphene (oxygen content of graphene sheets) on electrical property of graphene-PMMA nanocomposites. Electrical percolation threshold increases with increasing the oxygen content of graphene sheets. PMMA composites with the lowest oxygen content in graphene (graphene-13.2) show a dramatic increase in electrical conductivity of over 12 orders of magnitude, from 3.33×10^{-14} S/m with 0.4 vol. % of graphene to 2.38×10^{-2} S/m with 0.8% of graphene. The conductivity reaches up to 10 S/m at 2.67 vol. % (**Figure 2.31**). This rapid transition indicates the formation of an interconnected graphene network. In addition, composites with the lowest oxygen content (graphene-13.2) in graphene exhibit much higher conductivity, in the percolation transition range than composites with higher content of oxygen (graphene-9.6 & graphene-5.0). The presence of oxygen-

containing groups on graphene has been proved to disrupt its graphitic sp^2 network and decrease its intrinsic conductivity. Generally, the higher the oxygen content, the lower the intrinsic conductivity.

Table 2.4. Electrical and thermal properties of graphene/polymer nanocomposites.

Matrix	Filler	Filler loading (wt% ^a , vol% ^b)	Fabrication process	Electrical properties		Thermal properties		Reference
				Percolation threshold (wt% ^a , vol% ^b)	Surface resistance ^a (Ω) / Electrical conductivity ^b ($S m^{-1}$)	% increase in thermal conductivity	Thermal resistivity ^a ($M\Omega$) / Thermal Conductivity (W/mK)	
Epoxy	f-GP ¹	1.5 ^a	<i>In situ</i>			~25		53
	f-GP ¹		<i>In situ</i>	0.244 ^b				51
	CRGO ²		<i>In situ</i>	0.52 ^b				4
	Graphene	1.0 ^a	<i>In situ</i>			23.8		64
PMMA	CRGO ²		<i>In situ</i>	0.62 ^b				87
	f-GO ³		<i>In situ</i>	0.26 ^b	2.47×10^{-5} b			88
PE	TRGO ⁴		Solution blending	0.16 ^b				36
	TRGO ⁴	1.0 ^a	Solution blending		2×10^8 a			35
	Graphene		<i>In situ</i>	3.8 ^b				59
PU	f-GP ¹	0.5	Melt blend.	>0.5 ^b				38
			Sol. blend.	<0.3 ^b				
			<i>In situ</i>	>0.5 ^b				
PVA	f-CRGO ⁵	3.0 ^a	Solution blending	0.37 ^b	0.9×10^{-2} b			31
PVDF	TRGO ⁴		Solution blending	4.5 ^a				33
	TRGO ⁴		Solution blending	0.016 ^b				89
PBT	Graphene	0.5					760	57
		1.0	Solution blending				50	
PANI	CRGO ²	10.0 ^a	Solution blending		8.38×10^{-4} a 11.92×10^{2} b			90

¹ Functionalized graphene, ² Chemically reduced GO, ³ Functionalized GO, ⁴ Thermally reduced GO, ⁵ Functionalized chemically reduced GO,

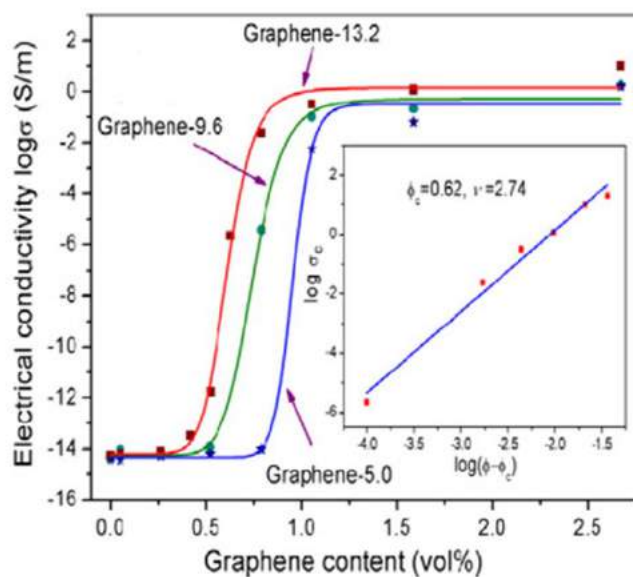


Figure 2.31. Electrical conductivity of graphene/PMMA composites as a function of graphene content.³⁶

Wang et al.⁹¹ have reported the ability to tailor the electrical properties of the composites by altering the GO oxidation state. Each energy barrier, from either the GO surface groups or the contact between GO platelets, possesses a characteristic voltage above which the electrons can tunnel through. The total switching voltage of the composites should be the sum of those characteristic voltages. Thus adjusting the oxidation state of GO can affect the energy barriers from surface groups⁹² and eventually change the total switching voltage. By increasing the reduction temperature the switching voltage can be increased. It is suggested that this was due to a reduced number of oxidized surface groups, as well as the number of energy barriers. The saturated conductivity can also be changed by tuning the oxidation state of GO. This is likely due to the rearrangement of functional groups on the GO surface during the heat treatment process. Another study reported the low percolation threshold of 0.16 vol% and the highest electrical conductivity of ~ 64.1 S/m at 2.7 vol % for PMMA-RGO composites, prepared by a simple latex technology approach where self-assembly of positively charged PMMA latex particles and negatively charged graphene oxide sheets through electrostatic interactions, followed by hydrazine reduction.⁸⁷ The effect of temperature on electrical conductivity of graphene/PVDF composite was investigated.⁹³ The EG/PVDF composites showed a gradual increase in resistivity with temperature followed by a sharp increase when

the melting point of PVDF is reached. As the temperature approaches the melting point of the polymer, the distance between particles increases (due to volume expansion of the matrix), leading to a sharp increase in resistance. In contrast, the TRGO-PVDF nanocomposites show its resistivity decreases gradually with temperature with a dramatic decrease in resistivity above the melting point. This negative temperature coefficient behaviour of TRGO/PVDF composite was attributed to the higher aspect ratio of TRGO which leads to contact resistance predominating over tunnelling resistance. Usually, contact resistance can predominate as the number of contacts increases either because of an increase in the number of particles or an increase in the aspect ratio.

Thermal conductivity

Thermal conductivity (K) of the material is governed by the lattice vibrations (phonon). High thermal conductive graphene ($\sim 3000 \text{ W m}^{-1} \text{ K}^{-1}$, at room temperature) has been used as filler to improve the thermal conductivity and thermal stability of polymer. CNTs show similar intrinsic thermal conductivity, but sheet-like 2D structure of graphene may provide lower interfacial thermal resistance and hence produce better conductivity enhancement in polymer composites.^{8, 85} Other factors such as aspect ratio, orientation and dispersion of graphene sheets will also affect thermal properties of composites. Thermal conductivity of graphene based composites with different polymer matrices such as epoxy^{19, 52-53, 60, 94-95}, PMMA^{36, 96}, PP⁵⁰, PC⁹⁷ etc. has been extensively investigated (**Table 2.3**). Shahil et al.⁹⁸⁻⁹⁹, have fabricated thermal interface materials (TIMs) based on epoxy and a mixture of graphene and multilayer graphene (MLG). TIMs showed cross plane thermal conductivity (K) up to $\sim 5.1 \text{ W/mK}$ at 10 vol% loading, which corresponds to thermal conductivity enhancement of $\sim 2400\%$ compared to pristine epoxy as shown in the **Figure 2.32**. This unusual enhancement has been explained by means of high intrinsic thermal conductivity and geometrical shape of graphene/MLG flakes, low thermal resistance at the graphene/matrix interface, high flexibility of MLG flakes and optimum mix of graphene and MGL with different thickness and lateral size. Chatterjee and co-workers⁵³, prepared amine functionalized graphene by mixing dodecylamine with expanded graphene nanoplatelets (EGNPs) under N_2 atmosphere at 80°C . These functionalized EGNPs were dispersed in epoxy using three-roll mill calendaring and resulting nanocomposites showed steady increase of thermal conductivity with EGNPs loading. At 2 wt. % of EGNP loading an increment by

36% is observed as compared to pristine epoxy. The increasing trend promises higher thermal conductivity at larger EGNP concentrations. Since efficient heat propagation in EGNPs is mainly due to acoustic phonons, a uniform dispersion and network of EGNPs in the polymer matrix may contribute to the steady increase in thermal conductivity in the composites.

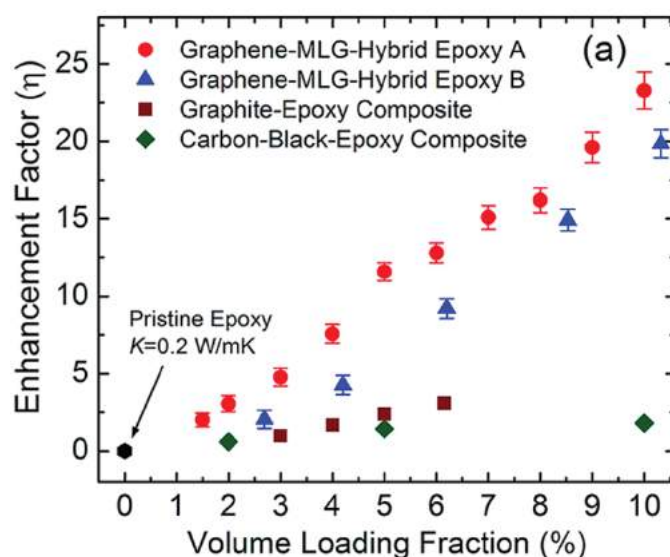


Figure 2.32. Thermal conductivity enhancement factor as a function of the filler volume loading fraction.⁹⁸

Teng and co-workers⁵² have reported significant increase in thermal conductivity of epoxy composites with the increasing graphene content, which is superior to the SWCNT/epoxy composites, as illustrated in **Figure 2.33(a)**. Further, chemically modified graphene (CMG)/epoxy composite exhibited the highest improvement in thermal conductivity. For example, at 1 phr loading of CMG, thermal conductivity of composite improved by 208.7%. This significant enhancement can be because of better graphitic structure of graphene (non-covalent functionalization can preserve the structure of graphene compared to thermal reduction), reduced interfacial thermal resistance due to strong interactions between CMG and epoxy matrix, and increased contact area between graphene and the matrix caused by homogeneous dispersion of CMG in the matrix. A hybrid of graphene (MGP) and multi wall carbon nanotubes (MWCNTs) was fabricated to generate the synergetic effect on thermal conductivity of epoxy nanocomposites by Yang et al.⁶⁰ As seen in the **Figure 2.33(b)**, MGP/epoxy composite showed the least improvement in thermal conductivity of all composites. By contrast, the hybrid carbon

fillers/epoxy composite exhibited a significant improvement in thermal conductivity ($\sim 147\%$). They proposed that this synergetic effect originated from the contact geometry changes by bridging planar graphene sheets by the MWCNTs which increases the contact surface area within hybrid nanofillers and decreased interfacial resistance within hybrid nanofillers resulting in reduced phonon scattering. A synergistic effect of hybrid of graphite nanoplatelets (GNP) and SWCNTs was reported by Yu et al.¹⁰⁰ The experimental data showed a pronounced maximum of thermal conductivity of $1.75 \text{ W m}^{-1} \text{ K}^{-1}$ at a GNP: SWCNT filler ratio of 3:1 (7.5 wt % GNPs and 2.5 wt % SWNTs in epoxy).

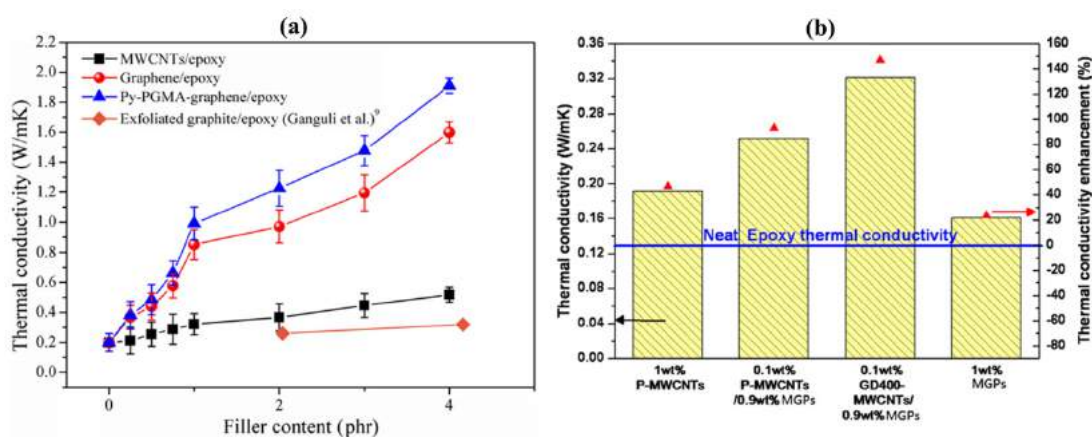


Figure 2.33. (a) Thermal conductivity with various filler contents of MWCNTs/epoxy, graphene/epoxy, and Py-PGMA-graphene.⁵² (b) Thermal conductivity of epoxy composites with 1 wt% p-MWCNTs, 0.1 wt% p-MWCNTs/0.9 wt% MGPs, 0.1 wt% GD400-MWCNTs/0.9 wt% MGPs and 1 wt% MGPs.⁶⁰

Other properties

Thermal stability is another important property that can be improved by embedding graphene in polymer matrices. Because of high thermal stability and layered structure of graphene, incorporation of it in polymer matrices can significantly improve their thermal stability and other thermal properties like flame retardancy, thermal expansion etc. A significant number of works has reported improved thermal stability of polymers using graphene and its derivatives.^{36, 69, 101-106} As it can be seen in **Figure 2.34**, inclusions of carbon nanofillers i.e., graphene nanosheets (GNS) and CNTs, into rigid polyurethane foam (RPUF) increase the T_g whereas decrease the $\tan \delta$ of PU.¹⁰² Both T_g and $\tan \delta$ interpret the mobility and movement capacity of polymer molecule chain segments. The presence of GNS and

CNTs highly impedes the polymer chain motion via strong interfacial interactions and acts as “physical crosslink” during the glass transition, which evidently improves the stiffness and heat resistance of the nanocomposites.¹⁰²⁻¹⁰³ Further in reference 102¹⁰², the observed amplitude of the variation in T_g and $\tan \delta$ is high for GNS nanocomposites compared with that of CNT nanocomposites (**Figure 2.35**), which is also ascribed to the greater interfacial interaction between the matrix PU and wrinkled GNSs with unique two-dimensional geometrical morphology.

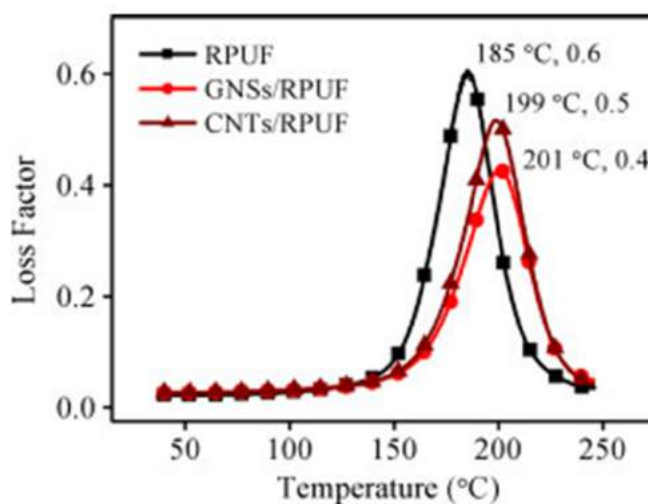


Figure 2.34. Temperature dependence of loss factor ($\tan \delta$) for pristine RPUF and GNS- and CNT-filled RPUF nanocomposites with 0.3 wt% content.¹⁰²

The use of polymer in high temperature applications limits by their degradation at low temperature as compared to ceramics or metals. The degradation behaviour of polymers is commonly evaluated in terms of three parameters: (1) the onset temperature, considered as the temperature at which the system starts to degrade, (2) the degradation temperature, considered as the temperature at which the maximum degradation rate occurs, and (3) the degradation rate, seen in the derivative weight loss as a function of temperature curve.² Graphene and functionalized graphene oxide improved the thermal degradation stability of several polymer matrices, such as epoxy¹⁰⁶⁻¹⁰⁷, HDPE⁸⁴, poly (arylene ether nitrile) (PEN)¹⁰¹, polycarbonate (PC)¹⁰⁸. In one study, the degradation temperature of PS composite increased with graphene content. A maximum increase of 16°C was observed for the 20 wt% composite (**Figure 2.35**).¹⁰⁹ However, non-reduced GO did not significantly influence the thermal stability of different polymers like polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), and high-impact polystyrene (HIPS). However, GO shows

some promise toward the fabrication of polymer nanocomposites in which decreased flammability is desired.¹¹⁰ Similar to SWCNTs, the negative coefficient of thermal expansion (CTE) of graphene can significantly lower the CTE of polymer matrix. Wang et al.¹¹¹ showed that the SWCNT and graphene have similar effect in decreasing CTE in epoxy matrix. More significant reduction of CTEs below T_g was observed for incorporation of 5% GO into epoxy. The reduction is as high as 31.7%. However, at above glass transition temperature (T_g), CTEs of the composites showed slight variation in comparison to the pristine resin.

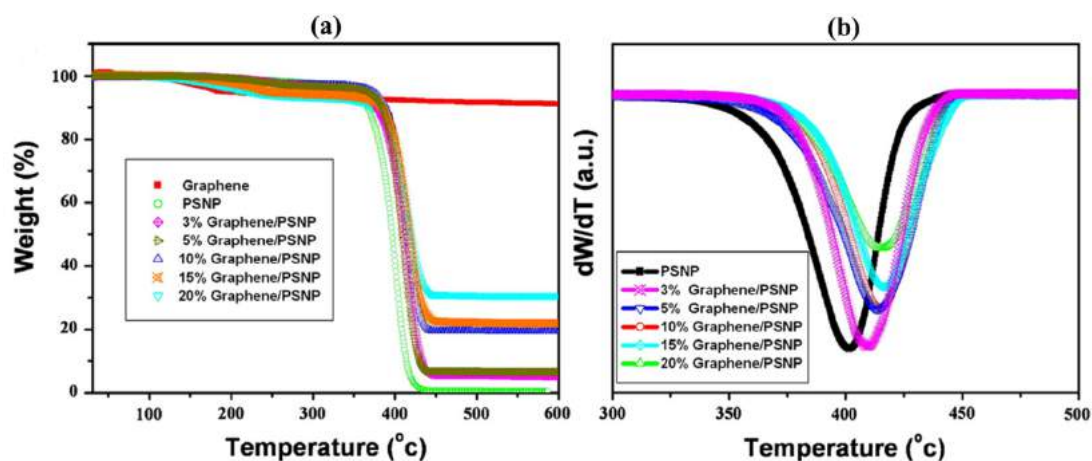


Figure 2.35. Thermal properties of the graphene/PS nanocomposites. (a) TGA and (b) DTG curves.¹⁰⁹

In addition to improved mechanical, electrical and thermal properties, incorporation of graphene can significantly reduce gas permeability of polymer composite relative to the pristine polymer. Various studies^{8, 112-115} showed that the reduction of gas permeability is probably associated with the high aspect ratio and surface area of graphene provides a tortuous path for the diffusing gas molecules, enhancing the gas barrier properties compared to pristine polymer. Pinto et al.¹¹⁶ investigated the resistance of PLA/graphene (GNP) and PLA/GO composites to oxygen and nitrogen. The gas permeability decreased by threefold towards oxygen and a fourfold towards nitrogen at 0.4 wt% loading of GO or GNP. Though, it could be expected that more planar configuration of GNP would be more efficient in creating a tortuous path for permeation than GO particles, this was not observed, and both fillers showed similar effects. They explained this as the absence of orientation of the GNP platelets along the film plane, which does not contribute to increasing the tortuosity in the direction perpendicular to the film plane. Kim et al.³⁸, reported

comparison study of various forms of graphene reinforced PU by different processing techniques. They have found that in situ polymerized TRGO was not as effective as solvent blended TRGO in reducing gas permeability. Further, the incorporation of isocyanate treated GO showed a 90% reduction in nitrogen permeability at 1.6 vol% loading. Detailed investigation by Chang group¹¹⁵, on permeability of oxygen and water through graphene reinforced PANI nanocomposites have revealed the significant improvement in barrier properties compared to that of the nanoclay reinforced PANI as illustrated in **Figure 2.36**.

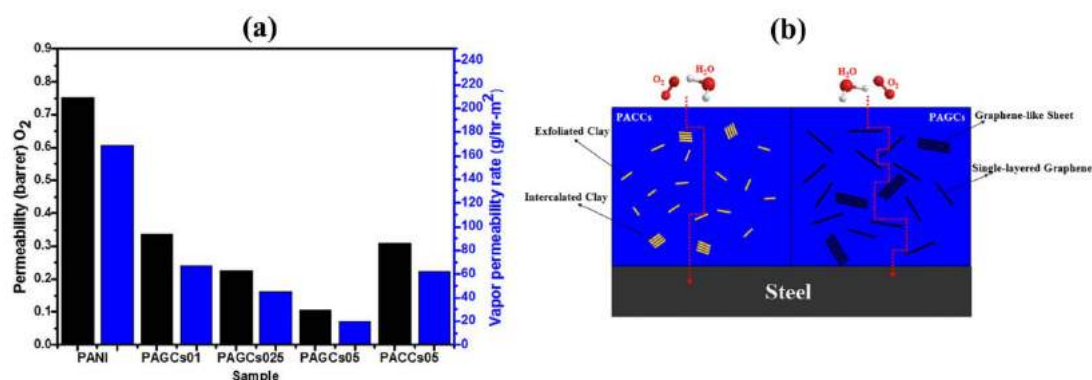


Figure 2.36. (a) Permeability and vapour permeability rates of PANI and nanocomposites (b) Schematic representation of O₂ and H₂O following a tortuous path through a poly(aniline)/graphene composites (PACCs) and poly(aniline)/clay composites (PAGCs).¹¹⁵

2.9.4 Graphene-CNTs hybrid-polymer nanocomposites

Carbon nanotubes (CNTs) and graphene which are representatives of one and two dimensional nanostructure have attracted considerable attention over last two decades due to their excellent properties and wide applications. Graphene, a single-atomic layer of carbon hexagons, can be stacked into graphite or rolled up into cylindrical CNTs. They are mutually complementary in both structure and properties and yet share many common properties such as ultrahigh mechanical strength and electrical conductivity. However, they have their own drawbacks. CNT have superior mechanical properties but must be dispersed uniformly and form a network to achieve sufficient percolation for electrical conductivity. On the other hand, graphene has remarkably high electron mobility at room temperature but causes problem of its restacking property.¹¹⁷⁻¹¹⁸ Zhang et al.¹¹⁹ classified the graphene-CNT

hybrids into three types, CNTs adsorbed horizontal to the graphene sheets (GNS), CNTs adsorbed perpendicular to the GNS and CNT wrapped with GNS. .

Such hybrid structures show excellence flexibility and stretching ability and is expected to have electrical conductivity and thermal dissipation in all directions. Further, irreversible agglomeration of graphene via van der Waals interaction is found to be hindered in the presence of CNTs.¹²⁰ In recent years, integrate them into a hybrid structure created a wide interest to establish synergistic effects between these two different carbon structures in composite materials.

Shin et al.¹²¹ fabricated PVA tough fibres by wet spinning of hybridized reduced GO flakes (RGOFs) and single-walled CNTs (SWNTs) into PVA solution. The fabricated fibres exhibit the toughness in the range of 480-970 Jg⁻¹, far exceeding toughness of silk or Kevlar (**Figure 2.37(a)**). This synergistic toughness enhancement arises for the optimal combination of SWNTs and RGOFs (1:1), and no synergistic toughness enhancement was observed for other ratios of carbon nanoparticles. The results show that this optimal ratio of SWNT and RGOF leads to a high degree of nanoparticle self –alignment (**Figure 2.37(b)**) and hinder RGOFs stacking during wet spinning which provides strong interaction with the PVA matrix, enhances crack deflection, and promotes plastic deformation (**Figure 2.37(c)**) of the stretched PVA.

Wang et al.¹²² prepared SWCNT, GO and their hybrid PVA fibres and reported high strength and high conductive PVA fibre with hybrid SWCNTs and GO at 2:1 ratio. Intercalation of GO sheets into CNTs forms a well dispersed GO-CNTs network in PVA matrix which facilitates the stress transfer between the nanocarbons and PVA molecules resulting synergistic enhancement of strength properties. In addition to strength, a better dispersion state enhances the conductivity of the fibres. One study reported a marked improvement in fracture toughness and flexural modulus for different ratios of CNT and graphene with the highest improvement for CNT:graphene ratio of 9:1.¹²³

Kumar et al.¹²⁴ have reported a remarkable increase in thermal and electrical conductivities of Polyetherimide (PEI) containing the hybrid ternary systems of GNPs and MWCNTs in equal amounts at a fixed loading of 0.5 wt%. In the case of thermal conductivity, composites containing hybrid fillers exhibited a 45% increase whereas composites with only GNPs or MWCNTs exhibited improvement of 22%

and 9%, respectively as compared to pure PEI. The surface resistivity of hybrid composite showed 8 orders of magnitude lower than that of a composite with 0.5 wt% GNPs alone and an order of magnitude lower than MWCNT/PEI composite. The formation of an interconnected hybrid network structure between MWCNTs and GNPs may facilitate the better electron transport throughout the polymer result in reduced surface resistivity. Another possible reason for reduced surface resistivity of the hybrid composite was improved dispersion and damage prevention of carbon nanotubes in the presence of graphite nanoplatelets during the fabrication process. The preserved long length of nanotubes can bridge the gap between graphite nanoplatelets thereby allowing the greater mean free path for the electron flow. Synergistic effect of hybrid graphene-CNTs in various polymer matrices has been reported in literature.^{60, 125-127}

2.9.5 Conclusions

We have reviewed the recent advances in fabrication, properties and potential applications of graphene-polymer nanocomposites. We have also discussed the recent studies and progress synergistic property improvement in hybrid graphene-CNT polymer nanocomposites. Based on the review, it is clear that the reinforcement of graphene and its derivatives in polymer matrices has shown very promising results in improving mechanical strength and elastic modulus, enhancing electrical conductivity at a low percolation threshold, increasing thermal conductivity, stability and flame resistance, and reducing gases and water vapour permeation. All of these enhancements have a great potential for applications in many fields either as structural or functional materials. For example, high strength and light weight structural polymer composites can be used in aerospace and automobile industries. Mechanically reinforced thin film composites find their applications in petrochemical and biomedical industries. Thermally conductive and stabilized composites can be used in the structures requiring thermal management. Electrically conductive composites have been widely used for making various sensors, conductive electrode for solar cells, antistatic coatings, electromagnetic interference shielding, etc.

However, to further commercialize graphene-polymer composites, many technical challenges need to be overcome. Most importantly, synthesis routes for mass production of graphene are urgently required. The preparation and transfer of

high quality graphene is still not practicable in a cost effective manner. At present, large amount of graphene is prepared by exfoliation followed by reduction of graphite oxide. Usually, sonication and thermal shock techniques are employed to exfoliate GO but they can reduce the aspect ratio of exfoliated GO, and adversely affect the reinforcing efficiency. Moreover, various defects and impurities are often introduced into graphene during the processing and these impurities may strongly influence the electrical, mechanical and thermal properties of graphene. In addition, structure, aspect ratio, surface chemistry and number of layers of GO/RGO are all dependent on the exfoliation and reduction procedures. Therefore, reinforcement of polymer with GO or reduced GO may exhibit undesirable properties as compared to pristine graphene-polymer composites. As such, methods for synthesis of graphene at low fabrication cost are urgently required.

Generally, the properties of polymer composites depend mainly on the dispersion state of discrete filler phase in continuous polymer matrix phase. The restacking of flat graphene sheets during fabrication makes uniform dispersion difficult and limits the available surfaces to interact effectively with polymer matrix, deteriorating the reinforcing effectiveness. Strong interfacial interactions between graphene and the host polymers and interaction within the graphene sheets are other important factors to be considered in fabricating high performance composites. Further, property enhancement of graphene-polymer composites can be achieved by morphological control of graphene. Wrinkles and surface roughness in graphene may increase the reinforcement due to mechanical interlocking but may degrade electrical and thermal properties. Therefore, the core issues such as homogeneous dispersion of graphene sheets, their connectivity and orientation, interfacial interaction with host polymer matrix still deserve further research. In addition, possible risk associated with use of graphene and its derivatives need to be evaluated.

2.9.6 References

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3 Preparation of Graphene Oxide-Epoxy Nanocomposites with Significantly Improved Mechanical Properties

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3.1 Prelude

The oxygen-containing groups on GO sheets give hydrophilic characteristics to the graphene oxide layers and bulk graphite oxide can also be exfoliated into individual graphene oxide sheets via simple sonication in an organic solvent such as N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) or in water without the need of additional chemical functionalization. The large-scale preparation of graphene oxide dispersions in organic solvents is highly desired facilitating the fabrication and practical use of graphene oxide-based polymer nanocomposites.

Further, the functional groups bound to the GO surface may improve interfacial bonding between GO and polymer matrix which plays a vital role in the improvement of nanocomposite mechanical properties. Thus, by combining remarkable mechanical properties and low costs, 2D graphene oxide sheets are expected to offer promising nanoscale filler for the next generation of nanocomposite materials.

In this paper, GO-epoxy nanocomposites were fabricated and characterised. Results have shown that addition of tiny amount of GO into epoxy matrix can significantly enhance the mechanical properties of the epoxy. Further, we have found that GO significantly hindered the cure reaction in the epoxy system.

***** This chapter includes an addendum. It contains additional data which has been collected after publishing of the paper. This additional work further confirmed the optimum GO loading (0.1 wt%) for enhancement in mechanical properties.***

3.2 Statement of Contribution

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of the journals or other publications and (c) the head of the responsible academic unit, and
5. they agree to the use of publication in the student's thesis and its publication on the Australia Thesis Database consistent with any limitation set by publisher requirements.

In the case of this chapter:

Preparation of graphene oxide/epoxy nanocomposites with significantly improved mechanical properties

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Mingchao Wang	paper writing
Graeme George	Overall supervision of the project, paper writing
Eric Waclawik	paper writing
Nunzio Motta	paper writing
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I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

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16/6/15

Name

Signature

Date

Abstract

The effect of graphene oxide (GO) on the mechanical properties and the curing reaction of Diglycidyl Ether of Bisphenol A/F and Triethylenetetramine epoxy system was investigated. GO was prepared by oxidation of graphite flakes and characterized by spectroscopic and microscopic techniques. Epoxy nanocomposites were fabricated with different GO loading by solution mixing technique. It was found that incorporation of small amount of GO into the epoxy matrix significantly enhanced the mechanical properties of the epoxy. In particular, model I fracture toughness was increased by nearly 50% with the addition of 0.1 wt% GO to epoxy. The toughening mechanism was understood by fractography analysis of the tested samples. The more irregular, coarse and multi-plane fracture surfaces of the epoxy/GO nanocomposites were observed. This implies that the two-dimensional GO sheets effectively disturbed and deflected the crack propagation. At 0.5 wt% GO, elastic modulus was ~35% greater than neat epoxy. Differential scanning calorimetry results showed that GO addition moderately affect the glass transition temperature (T_g) of epoxy. The maximum decrease of T_g by ~7°C was shown for the nanocomposite with 0.5 wt% GO. DSC results further revealed that GO significantly hindered the cure reaction in the epoxy system.

Key words: A. Graphene oxide, B. Epoxy nanocomposite, C. Mechanical performance, D. Cure reaction

3.3 Introduction

Graphene, an atomically thick nanosheet of sp^2 -hybridized carbon atoms arranged in a hexagonal two-dimensional (2D) lattice, has generated great interest during the past few years owing to several unique and outstanding properties. Graphene has shown a great potential for various applications such as supercapacitors, lithium ion battery and in high performance polymer composites. Considerable work has already been reported, showing greatly improved electrical, mechanical and thermal properties of neat polymer when reinforced with graphene.¹⁻⁴ For instance, Rafiee *et al.*³ produced epoxy nanocomposites with graphene, single and multi-walled CNTs and compared the mechanical properties at weight fraction of 0.1%. The Young's modulus of their graphene nanocomposite was ~31% greater than the pristine epoxy as compared to ~3 % for single-walled carbon nanotube

(CNT). Similarly, model I fracture toughness of epoxy/graphene nanocomposite showed ~53% increase compared to ~20% improvement for multi-walled CNT. The superior property improvement of graphene over CNTs was related to the 2D geometry, high specific surface area and better graphene-polymer matrix adhesion due to wrinkled surface texture. However, several key issues need to be resolved in order to attain optimal property enhancement of graphene polymer composite. Similar to any other filler, dispersion and interfacial interactions are the main issues of graphene which directly influence the properties for their composites. Graphene sheets usually tend to form aggregates in solvents and polymer matrices due to strong graphene-graphene intermolecular van der Waals forces consequently this limits dispersion and exfoliation.⁵ Poor dispersion and exfoliation of graphene significantly lowers their efficiency as reinforcement. Furthermore, the chemically inert and atomically smooth structure of graphene is highly incompatible with polymer matrix which limits load transfer from polymer matrix to graphene.⁶ Hence, homogeneous dispersion of graphene into the matrix, and the strong interfacial interactions between the graphene and the matrix are required in order to efficiently improve the properties of the host matrix.⁷

Compared to graphene, graphene oxide (GO) contains a range of reactive oxygen functional groups such as carboxylic acid, epoxy and hydroxyl group which offer several advantages over graphene. For example, GO is readily dispersible in water, and several organic solvents and polymers.⁸ Moreover, functional group attached on the GO surface can make strong interactions with polymer matrix. In addition, bulk quantities of GO can be easily produced by chemically oxidising graphite. Thus, recently several studies have used GO rather than graphene as reinforcing filler for polymer composite.⁹⁻¹¹ However, GO is an insulating material with lower stiffness and strength compared to pristine graphene. Suk *et al.*¹² reported that the Young's modulus of monolayer GO is 207 ± 23.4 GPa which is only 20% of the value for graphene. Significant toughness and fatigue life improvements through the addition of GO sheets to an epoxy system have been established.¹³ The addition of 1wt% GO to an epoxy led to the significant enhancements in flexural strength, flexural modulus and impact strength.¹⁴ Wang *et al.*¹⁵ reported the incorporation of 0.3% of GO into polybenzimidazole (OPBI) enhanced the polymer's Young's modulus by 17%, tensile strength by 33% and toughness by 88%. The extent of

oxidation of GO was tailored and its effect on the mechanical performance of polyvinyl alcohol (PVA) has also been investigated. The results showed that the less oxidized GO was more effective than fully oxidized GO in reinforcing PVA.⁸ The less oxidized GO could possess higher intrinsic mechanical properties with fewer defects which could be the reason for better enhancement of mechanical performance of PVA nanocomposites.

Epoxy resins are the most important thermosetting materials used in various industrial applications such as in automobile, aerospace, defence *etc.* The study of curing behaviour of epoxy systems is very important because of its close relation between glass transition temperature, mechanical properties and their potential applications. DSC is one of the most widely used techniques for the analysis of thermal and curing behaviours of thermosetting systems.¹⁶ In the literature, the cure behaviour of epoxy/carbon filler systems has been reported. Qui *et al.*¹⁶ studied the effects of GO on the curing behaviour of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) cured with 4,4'-diaminodiphenylsulfone (DDS) epoxy system. They showed that the oxygen functional groups on the surface of GO acted as catalysts and facilitated the curing reaction and the catalytic effect increased with the GO content. Bortz *et al.*¹³ reported similar effect of GO on DGEBA cured with 1,2-diaminocyclohexane (DACH). The acceleration effect has been explained by an increase of oxygen functional groups which could produce a catalytic effect on epoxide ring opening, resulting in higher reaction rates. Teng and co-workers¹⁷ claimed a hindrance effect of graphene on the cure reaction of the DGEBA/DDS epoxy system. In contradiction with Teng's work, Park *et al.*¹⁸ reported a catalytic effect of graphene to speed up the cure reaction rate of di-functional DGEBA/Diethyltoluenediamine (DETDA) epoxy system. Both accelerating¹⁹⁻²¹ and retardation²² effect of CNT on different epoxy systems have been reported by other authors.

However, to date, a relatively limited number of studies have reported on evaluating mechanical performance of GO incorporated epoxy composite and effects of GO on the curing kinetics of epoxy. In the present work, we report the effect of GO on mechanical and thermal behaviour of epoxy nanocomposites with variation of GO weight fraction. Results showed that the modulus, strength and toughness are all simultaneously improved. It was also revealed that GO had a significant influence on

the epoxy-amine curing reaction thereby reducing the glass transition temperature of the cured epoxy matrix.

3.4 Experimental

3.4.1 Materials

Epoxy resin (Araldite GY 191) used for this study is Diglycidyl Ether of Bisphenol A/F (DGEBA/F) and the curing agent (Hardener HY 956) is a low viscosity aliphatic polyamine (Triethylenetetramine/TETA). Both epoxy resin and curing agent were supplied by CG composites, Australia. Graphite flakes and the other chemicals used such as KMnO_4 , H_2SO_4 , H_3PO_4 , HCl , H_2O_2 , Acetone, Ethanol and dimethylformamide (DMF) were purchased from Sigma Aldrich (pvt) Ltd, Australia.

Preparation of graphene oxide

GO was prepared by oxidation of graphite flakes according to the method described by Marcano *et al.*²³ In brief, a mixture of graphite and KMnO_4 (Ratio of 1:6) was added into a beaker containing mixture of H_2SO_4 : H_3PO_4 (9:1) acids. Then the reaction mixture was stirred while heating at 50°C for 12 h. The reaction mixture was cooled down to room temperature and poured onto ice with 3 ml of 30% H_2O_2 . Then the mixture was sieved through a metal US standard testing sieve (250 μm). The filtrate was centrifuged at 4000 rpm for 30 minutes. The precipitate was washed with DI water, HCl and ethanol. For each wash, the mixture was sieved through US standard testing sieve followed by centrifuging at 4000 rpm for 30 min. The final precipitate was dissolved in DI water and sonicated for 1 h. The sonicated GO dispersion was placed in a deep freezer for 24h followed by freeze drying at -51°C under vacuum for 72h.

Preparation of graphene oxide-epoxy nanocomposites

A homogeneous dispersion of GO in acetone (1mg/ml) was obtained by employing an ultrasonicator at high amplitude for 1 h. Then a certain amount of epoxy resin was added and the mixture was stirred for 15 min on a magnetic stirrer. Acetone was evaporated by stirring the mixture at 40°C for few hours on a hot plate with a magnetic stirrer. The mixture was placed under vacuum at same temperature overnight for the complete removal of acetone. The stoichiometric amount of hardener was added to the epoxy-GO mixture at room temperature and mixing was

carried out in a high speed shear mixer (Thinky planetary mixer) at 2000 rpm for 5 min. The mixture was then poured into Teflon coated moulds after degassing in a vacuum oven for 30 min. Samples were pre-cured at room temperature for 24h and post-cured at 90°C for 6 h.

3.4.2 Characterization

Graphene oxide

X-ray diffraction (XRD) powder patterns were taken on a conventional X-ray diffractometer (XRD, PANalytical Cu MPD) using Cu α radiation. Raman spectra of bulk graphite and GO were recorded from 1250 to 3000 cm^{-1} on a Renishaw inVia Raman Microscope using a 532 nm edge filter laser beam. IR spectra were obtained using FTIR 5700 Nicolet Diamond ATR spectrometer. The spectrum resolution was 4 cm^{-1} in the range from 800 to 4000 cm^{-1} . 64 scans were performed to get the average spectrum. X-ray photoelectron spectroscopy measurements were performed with a Kratos Axis ULTRA X-ray photoelectron spectrometer (XPS) using monochromatic Al- α radiation ($h\nu = 1486.6$ eV). CasaXPS v 2.3.16 software was used to perform curve fitting and to calculate the atomic concentrations. The microstructural characterizations were performed using a JEOL-7001F field-emission scanning electron microscope (FESEM) operated at 15 kV and a JEOL 1400 transmission emission microscope (TEM) operated at 120 kV. Dry GO powder was used for the FESEM analysis. Clear solution of GO in DMF was dropped cast onto carbon coated copper TEM grid for TEM analysis. Samples for atomic force microscope (AFM) imaging were prepared by depositing clear solution of GO (in DMF) on freshly cleaved mica surface. AFM images were taken using a BMT multi-scan AFM with silicon tip. Tapping mode was applied to get the topography of the GO flakes at the scan rate of 1.2 Hz with surface area of $3 \times 3 \mu\text{m}^2$.

Epoxy nanocomposites

Single-edge-notch bending (SENB) specimens were fabricated according to the ASTM D5045-99 standard. A fresh razor blade was utilized to prepare a pre-crack by gently tapping it over a starter notch. Load displacement curves were obtained using Instron tensile machine with the 2 kN load cell at constant cross head speed of 0.5 mm/min. Plane-strain fracture toughness (K_{IC}) was calculated using the load vs. cross head displacement curves as follows;

$$K_Q = \left(\frac{P_Q}{BW^{1/2}} \right) f\left(\frac{a}{W}\right) \quad (6)$$

where P_Q is the maximum load on the load-displacement curve for the SENB specimen; B , W and a are the thickness, the width and the crack length of the specimen, respectively. The term a/W was in between 0.45 to 0.55 for all our samples.

For SENB samples, f is expressed as

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]^*}{(1+2x)(1-x)^{3/2}} \quad (7)$$

Dog-bone shaped tensile specimens were prepared according to the ASTM D638-10 standard. Tensile strength and elastic modulus were determined from stress-strain curve of composites using the Instron tensile machine with a 2 kN load cell at cross head speed of 0.5 mm/min. Both tensile and bending tests were performed at room temperature and at least five specimens were tested from each sample. The fractured surface images were obtained using FESEM (JEOL-7001F). The fractured ends of the specimens were mounted on aluminium stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. TEM and Raman mapping techniques were used to study the dispersion of GO in the epoxy matrix. TEM specimens were prepared by microtoming nanocomposite samples with thickness of 40-70 nm. The ultrathin films were placed on copper grids and examined with JEOL 1400 TEM using an accelerating voltage of 120 kV. For the Raman mapping study, a total of 2500 spectra were collected over a $25 \times 25 \mu\text{m}^2$ area of the composite surface and at the different depths through the Z axis (0-10 μm) from the surface. The spatial variation of the integrated intensity over the spectral range $1270\text{-}1440 \text{ cm}^{-1}$ (the location of the carbon related D-peak) and $1500\text{-}1700 \text{ cm}^{-1}$ (the location of the carbon related G-peak) were used to map the dispersion of the GO in the composite. The typical Raman spectra obtained from the GO regions and epoxy regions, respectively.

Thermal behaviour of the composites was investigated by differential scanning calorimetry (TA Instruments Q100 DSC). Experiments were carried out under nitrogen atmosphere at a scanning rate of $10^\circ\text{C}/\text{min}$ from 0 to 280°C . Glass transition temperature (T_g) was obtained from the heat flow curves of fully cured samples. To study the curing behaviour of nanocomposites, samples were prepared

*foot note: $x = a/W$

as follows. 5-10 mg of freshly prepared sample was added to the hermetic type DSC aluminium pan. Each sample was partially cured by placing in an oven at 90°C and taking out from the oven at different time interval (0, 5, 10, 15, 20, 25, 30 minutes). The heated samples were immediately put in the freezer to stop the reaction. Then, the heat flow curves were obtained for each sample at same experimental conditions used for T_g test as described above. The total heat of reaction (ΔH) was calculated using the heat flow curves and the conversion of reaction (α) was determined at each time, t ,

$$\alpha = 1 - \frac{\Delta H_t}{\Delta H_0} \quad (8)$$

3.5 Results and discussion

3.5.1 Characterization of graphene oxide

Prepared GO is highly hydrophilic and is readily dispersible in water and organic solvents such as DMF, acetone. XRD patterns of GO and bulk graphite are shown in **Figure 3.1(a)**. A characteristic sharp (002) peak of graphite stacking appeared at $2\theta = \sim 26.5^\circ$ with a corresponding interlayer spacing of ~ 0.34 nm. After oxidation of graphite to GO, the peak shifted to a lower angle at $2\theta = \sim 11.0^\circ$ with a matching spacing of ~ 0.8 nm which is similar to GO solids reported previously.²⁴⁻²⁵ The larger interlayer spacing of GO is due to the large number of polar groups generated between the layers of graphite during oxidation, in which the oxygen and carbon atoms are covalently bonded, leading to an increase in the graphite's crystal lattice length along axis c . The diffraction peak of graphite did not occur in the diffraction spectrogram of GO, indicating that the graphite had been completely oxidized. Raman spectra of graphite and GO are given in **Figure 3.1(b)**. The bulk graphite shows two intense bands centred at 1581 cm^{-1} (G band) and 2720 cm^{-1} (2D band). The G band is the response of the in-plane stretching motion of symmetric sp^2 C–C bond. The 2D band is the second order of the D band. A very tiny D band was observed for bulk graphite. This proved the absence of a significant number of defects in the graphite. In contrast, the Raman spectrum of the GO displays an intense D band centred at 1357 cm^{-1} and a G band at 1607 cm^{-1} . The D band arises from the disruption of the symmetrical hexagonal graphitic lattice as a result of internal structural defects, edge defects, and dangling bonds created by the

attachment of oxygen-containing functional groups such as hydroxyl and epoxide groups on the carbons.²⁶ D band intensity is directly proportional to the level of defects in the sample and can also be used as a gauge of degree of functionalization when graphene is chemically modified.²⁷

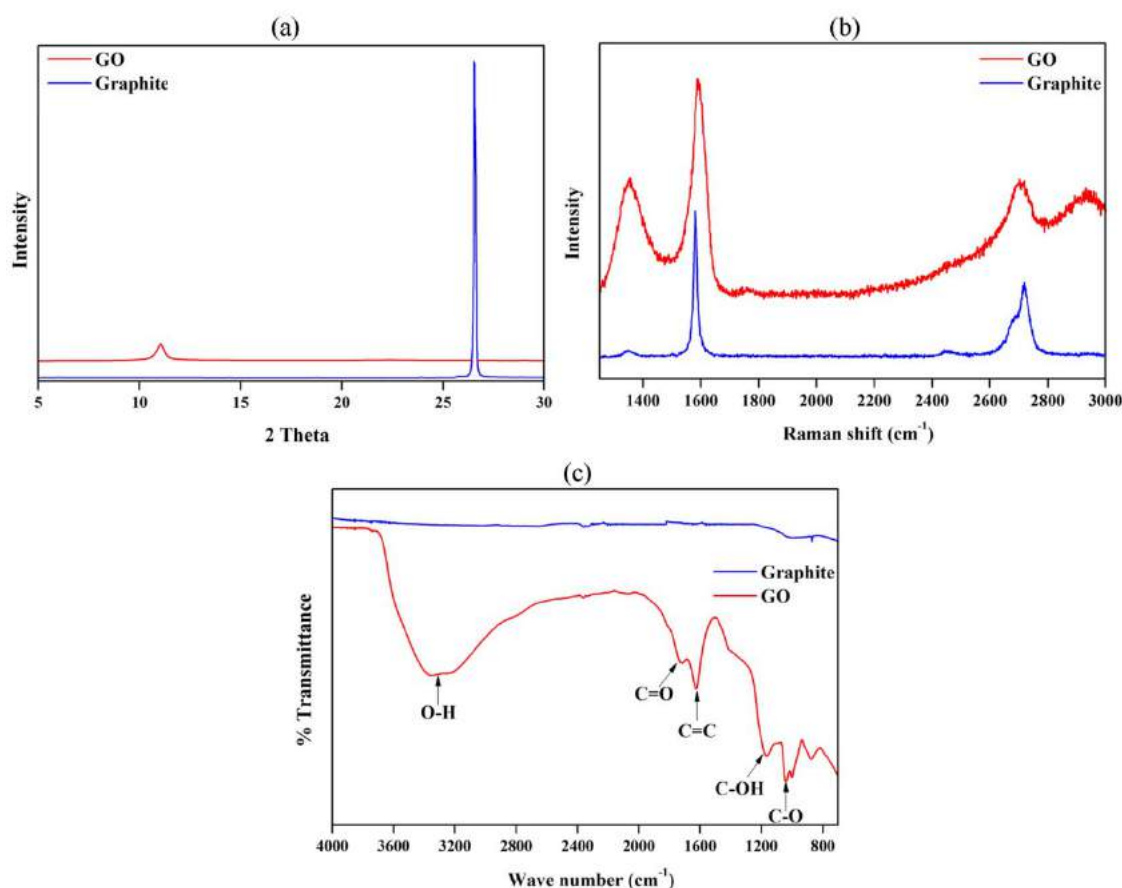


Figure 3.1. (a) XRD pattern; (b) Raman spectrum; (c) FTIR spectrum of graphite and graphene oxide.

Formation of functional groups during the chemical process was seen by FTIR analysis as shown in **Figure 3.1(c)**. There were no peaks observed in the spectrum of pristine graphite, indicating the chemically inert structure of bulk graphite. Chemical and structural changes of graphite upon oxidation are reflected in GO spectrum. A broad band around 3400 cm⁻¹ signifies stretching vibration of surface hydroxyls (~ 3400 cm⁻¹) and water absorption (~ 3200 cm⁻¹). The peaks are located at ~ 1720 cm⁻¹ (C=O stretching) from carbonyl and carboxylic groups, at ~ 1200 cm⁻¹ (C-OH stretching) from carboxylic groups and at ~ 1050 cm⁻¹ (skeletal C-O or C-C stretching) peak from carbonyl, carboxylic and epoxy groups, which confirms the presence of oxygen-containing functional groups.²⁸⁻²⁹ The peak at 1620

cm^{-1} can be assigned to the vibrations of the adsorbed water molecules and also the contributions from the skeletal vibrations of un-oxidized graphitic domains.³⁰

The C1s XPS spectrum of graphite before chemical treatment is shown in **Figure 3.2(a)**. The peak centred at 284.5 eV corresponds to graphitic carbon (non-oxygenated) and a weak π shake-up band is seen around 291 eV. The atomic composition of graphene oxide was obtained from the XPS survey spectrum and revealed the presence of C (66.6 at %) O (30.4 at %) and small amount of S, N and P (residues from the acids used for the oxidation process). The chemical composition detected for the GO is very similar to reported data in literature.^{26, 31-33} The detail C 1s and O 1s spectra are shown in **Figure 3.1(b) and (c)**, respectively, of the GO. The C1s XPS data of GO surface clearly displays the presence of four different kinds of carbon atoms. The binding energy of the non-oxygenated carbons (C-C and C-H) bonding are assigned at 284.7 eV. The binding energies at 285.8 eV, 287.5 eV and 288.9 eV can be assigned to carbons attached to carboxylic groups (C*-COOH), carbons in carbon-hydroxyl groups (C*-OH) and epoxy/ether (C*-O) and carboxylate carbons (O-C*=O), respectively.²⁵⁻²⁶ The peaks at 532.4 eV and 533.3 eV in the O1s spectrum of GO (**Figure 3.2(c)**) can be assigned to contributions from C=O* and C-O*-C/C-O*-H groups, respectively.²⁶ The peak seen at 534.1 eV may be due to the oxygen from water molecules. All these observations clearly indicate a high degree of oxidation of graphite by the oxidation process.

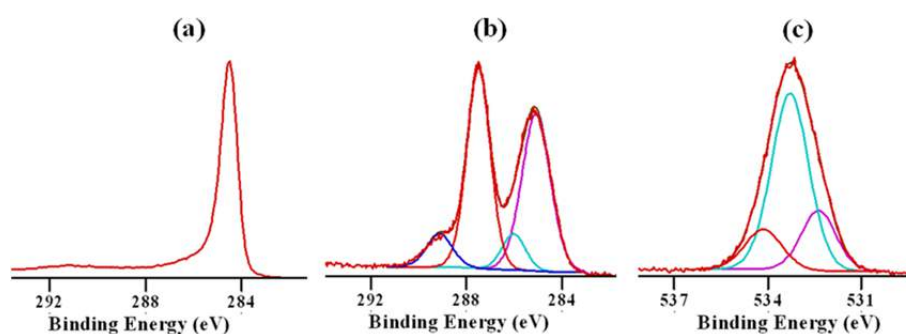


Figure 3.2. (a) C 1s XPS spectrum of graphite (b) C 1s and (c) O 1s XPS spectra of graphene oxide.

Figure 3.3(a) illustrates the typical SEM image of GO, indicating that GO consists of randomly aggregated, thin crumpled sheets closely associated with each other which are significantly different from graphite flakes. The platelets have lateral dimensions ranging from several hundred nanometers to several micrometers. The

morphology and structure of GO was further observed by TEM and the image is shown in **Figure 3.3(b)**. As is evident in **Figure 3.3(b)**, GO is highly electron transparent. It also clearly shows the wrinkled structure of single or few layers GO which is quite consistent with SEM morphology of **Figure 3.3(a)**.

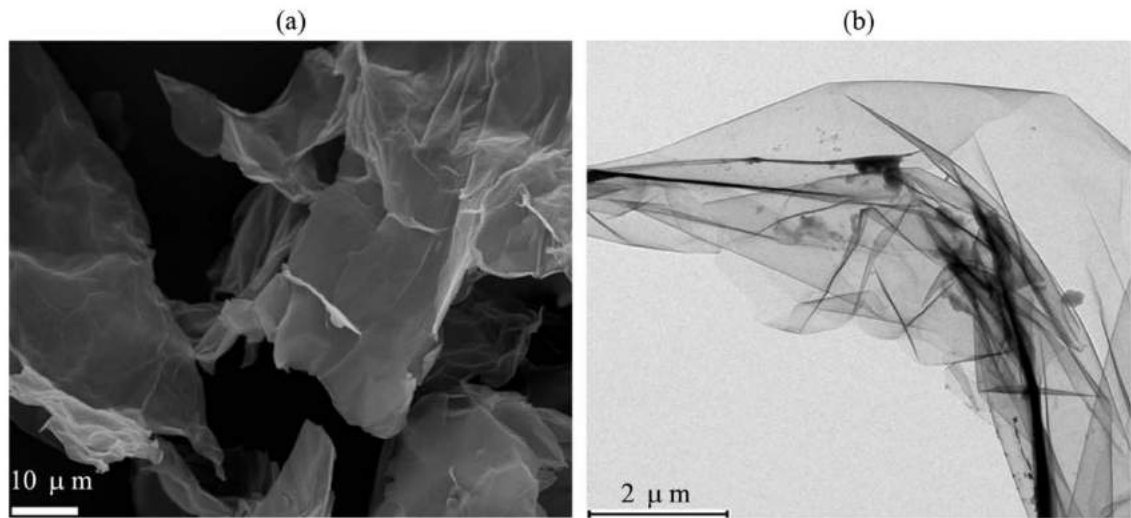


Figure 3.3. (a) FESEM (b) TEM images of graphene oxide.

From a tapping mode AFM image of GO on a mica substrate (**Figure 3.4**), the average thickness is ~ 1 nm. This value is very similar to the reported thickness of GO monolayer.³⁴⁻³⁶ Compared with the pristine graphene with a thickness of ~ 0.8 nm,³⁷ the higher thickness of as-made GO is due to the presence of the covalent C–O bonds at both top and bottom surfaces, distorted sp^3 carbon lattices and absorbed contamination.³⁸⁻⁴⁰

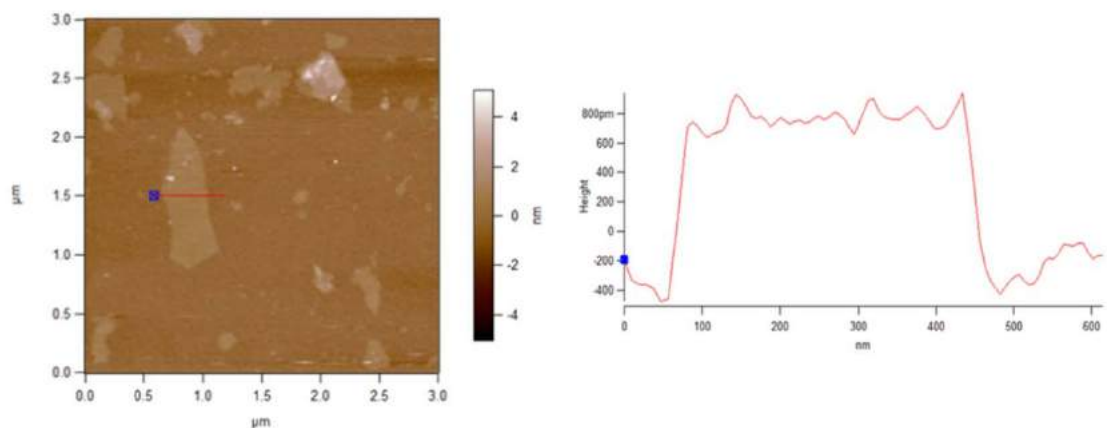


Figure 3.4. AFM image of graphene oxide.

3.5.2 Characterization of graphene oxide-epoxy nanocomposites

Dispersion of GO in epoxy resin

Raman mapping analysis was used to determine the dispersion of GO in epoxy matrix at different concentrations. The typical spectra obtained from the GO region and epoxy region are shown in **Figure 3.5**. The integrated intensity variation of carbon related-D peak ($1270\text{--}1430\text{ cm}^{-1}$) and G peak ($1500\text{--}1650\text{ cm}^{-1}$) (**Figure 3.5 (b)**) were used to map the dispersion of GO in the nanocomposites, however, for the results presented here only the integrated intensity of the D peak was used. **Figure 3.6** shows the intensity maps of the D peak over an area of $25\text{ by }25\text{ }\mu\text{m}$ for nanocomposites with (a) 0.1wt% (b) 0.3wt% (c) 0.5 wt% (d) 0.7 wt% GO at the depth of $4\text{ }\mu\text{m}$ from the surface. We show here results which are similar what we have found in several random regions of the sample. At low concentrations of GO, distribution of D peak intensity is uniform and in some areas D band is absent due to the lack of GO sheets. This implies that GO sheets are equally dispersed in epoxy matrix. As the GO loading increases, larger several micrometer sized GO agglomerates are visible illustrating poor dispersion of GO at higher loading (**Figure 3.6(c-d)**).

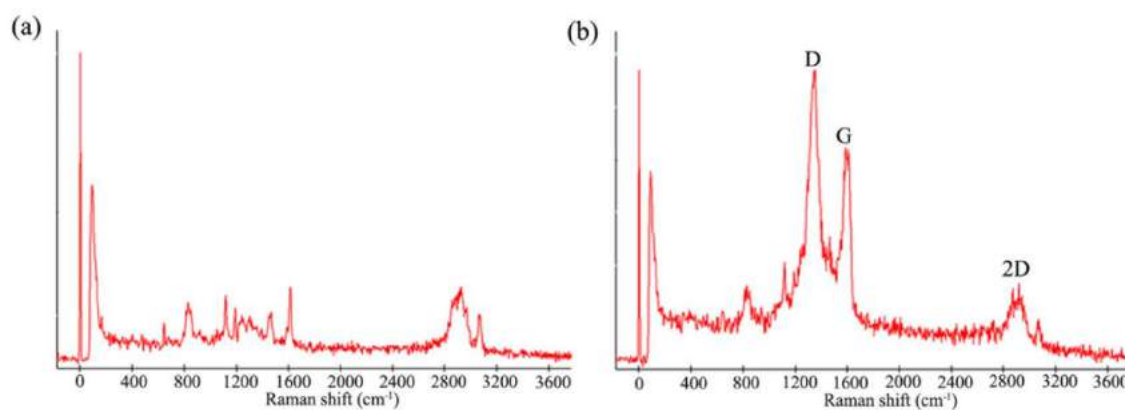


Figure 3.5. (a) Raman spectra obtained from epoxy-rich region (b) Raman spectra obtained from GO-rich region showing D, G and 2D bands.

Dispersion of GO in epoxy matrix was further studied by TEM analysis and **Figure 3.7** which shows the TEM image for a specimen with 0.5 wt% GO. As seen in **Figure 3.7(a)**, GO sheets exhibit considerably exfoliated and dispersed throughout the epoxy matrix although some small aggregations still exist. The number of GO layers could be observed by HRTEM of nanocomposite which was around 7-12 layers as can be seen in the **Figure 3.7(b)**.

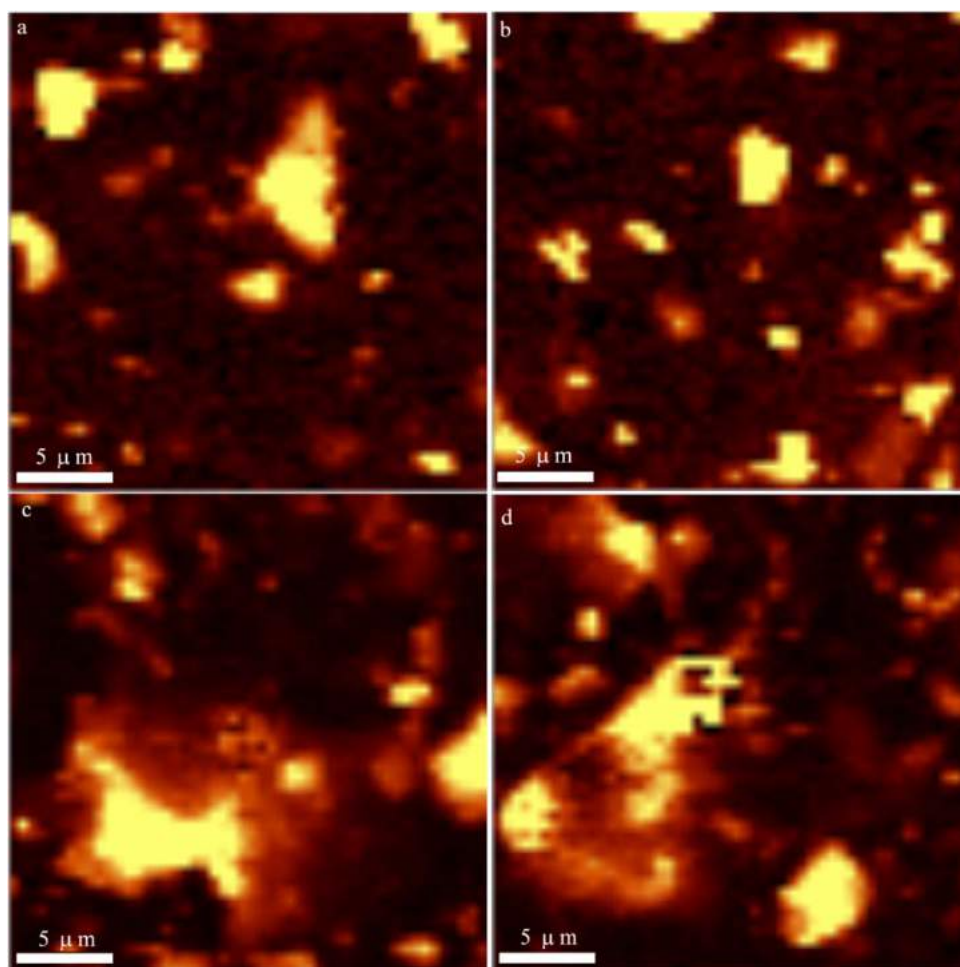


Figure 3.6. Distribution of GO in the epoxy matrix obtained by Raman spectroscopy for specimens at depth of 4 μm from the surface with GO loading (wt%) of (a) 0.1, (b) 0.3, (c) 0.5 and (d) 0.7.

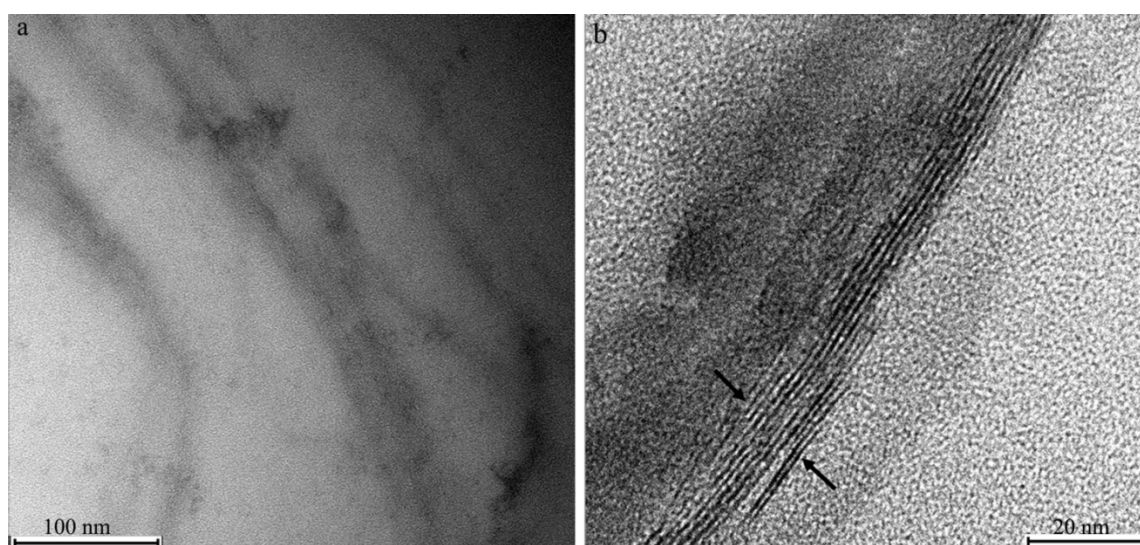


Figure 3.7. TEM images of graphene oxide-epoxy nanocomposites at 0.5% GO loading (a) at low (b) high magnification.

Mechanical properties

The mode I fracture toughness (K_{Ic}) of neat epoxy and the GO nanocomposites at various loading fractions was determined using the load-displacement curves and results are given in **Figure 3.8**. As it can be seen in the figure, K_{Ic} of neat epoxy is $\sim 1.34 \text{ MPa}\cdot\text{m}^{1/2}$, which is comparable to published literature.^{1, 4} The addition of 0.1 wt% GO into the epoxy matrix enhanced the K_{Ic} value of the nanocomposite to $\sim 2 \text{ MPa}\cdot\text{m}^{1/2}$, which corresponds to a $\sim 50\%$ increase in fracture toughness. It was found that for higher loading fraction, the enhanced ability of GO in K_{Ic} became weaker and come near the K_{Ic} value of neat epoxy with GO weight fraction of 0.5%. This decrease of the fracture enhancement could be a result of a saturation of the toughening effect and the degradation in the dispersion quality of GO at higher loading fractions as observed in Raman mapping and TEM studies (**Figure 3.6-3.7**).^{13, 41} Several researchers have observed the similar behaviour for the composites with higher filler loading fractions.^{1, 4, 13}

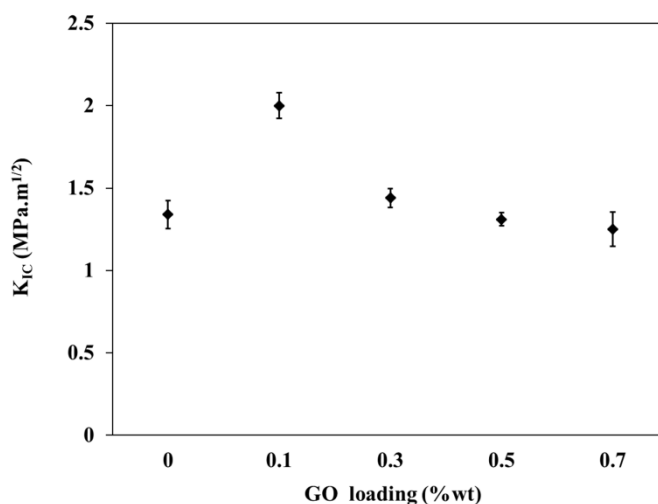


Figure 3.8. Plane-strain fracture toughness of graphene oxide-epoxy nanocomposites.

The fracture surfaces were observed using SEM to examine the fractured surface morphology and micrographs are presented in **Figure 3.9**. As shown in **Figure 3.9 (a)**, the fracture surface of neat epoxy is featureless with a smooth surface, consistent with its typical brittle fracture behaviour. The characteristic brittleness and low fracture toughness of cured epoxy are the result of high crosslink density of cured epoxy which causes low absorption of energy during fracture. With addition of GO, the fracture surface shows the more irregular, coarse and multi-plane surface features as seen in **Figure 3.9 (b-d)**, consistent with higher fracture

toughness of nanocomposites compared to neat polymer matrix. Generally, the higher the surface roughness, more fracture energy is dissipated.^{5, 13} This implies that the two-dimensional GO sheets could slow down the crack propagation by deflection of the propagating crack front. This crack deflection process creates new fracture surfaces, thus increasing the required energy for the crack propagation.^{3-4, 13, 42} However, it was observed that some micro-cracks on the fracture surface with addition of significantly higher amount of GO (see the black arrows in the **Figure 3.9 (d)**). This could indicate more flaws during the crack propagation in the nanocomposite which may result in early fracture of the nanocomposite. This should be the reason for decreasing of K_{IC} of nanocomposites at higher GO loading. According to Wang *et al.*,⁴¹ the enhancement of the epoxy toughness is strongly dependent on the size of the graphene sheet. The smaller the sheet size, better the reinforcement effect. The debonding/delaminating has been reported as one of the key elements of the toughening effect in epoxy matrix. The debonding/delaminating are able to trigger and promote the local plastic deformation of matrix to dissipate fracture energy and subsequently improved fracture toughness.⁵

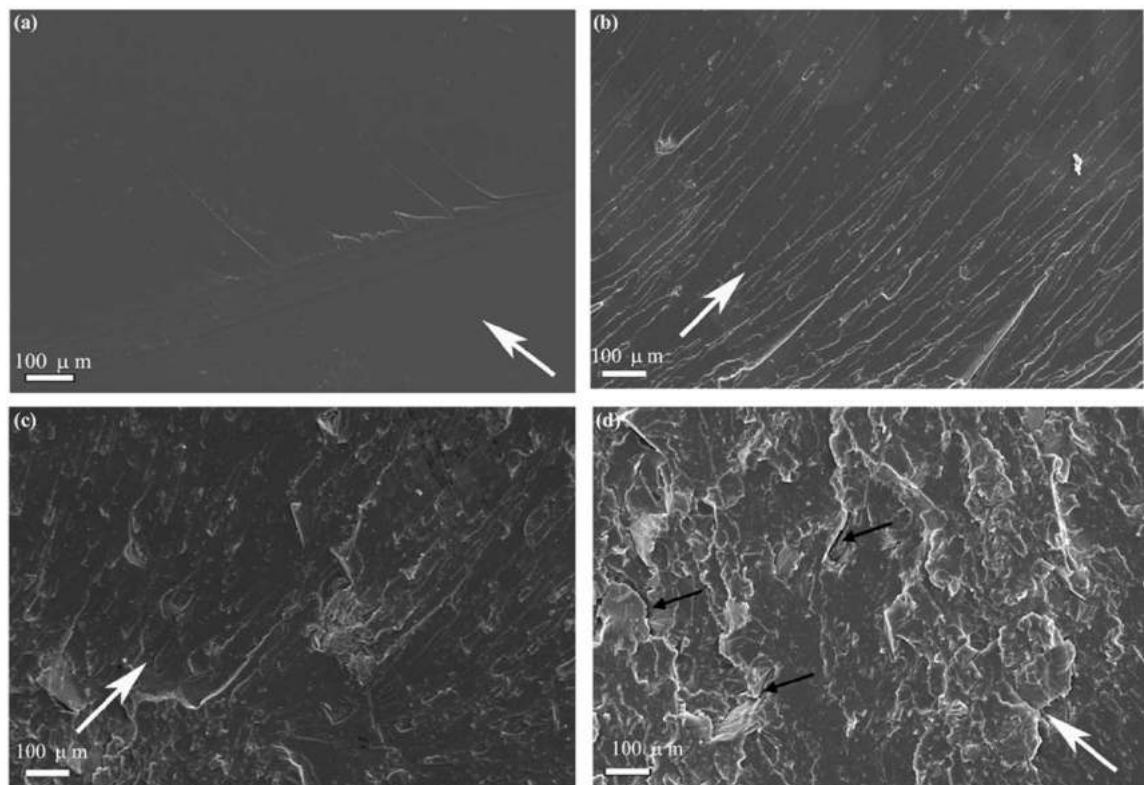


Figure 3.9. SEM images of fracture surfaces of SENB specimens: (a) neat epoxy, (b) 0.1 wt%, (c) 0.5 wt% and (d) 0.7wt% GO-epoxy nanocomposites. The white arrows at the bottom of the corners indicate the crack growth direction.

Figure 3.10 (a) shows variation of ultimate tensile strength and elastic modulus (average value of at least 5 specimens) of neat epoxy and the nanocomposites with different GO content and **Figure 3.10 (b)** presents the typical tensile stress-strain curves for neat epoxy and the GO/epoxy composite. From the **Figure 3.10 (a)**, it can be seen that elastic modulus and ultimate tensile strength of epoxy matrix increased with GO loading. Elastic modulus and tensile strength of neat epoxy are 1.28 GPa and 49.2 MPa, respectively, which are comparable to the values found in literature.² Elastic modulus was enhanced by ~28% at 0.1 wt % GO. Higher loadings also displayed increased tensile stiffness when compared to the neat epoxy but more modest than the weight fraction of 0.1% GO and showed the maximum improvement of 36 % in composite with 0.5 wt% GO compared to the baseline epoxy. Ultimate tensile strength showed a maximum enhancement of about ~7% in 0.1 wt% GO nanocomposite compared to control sample. **Figure 3.10 (b)** shows that as more GO was incorporated, considerably reduced strains at ultimate strength are observed. The decreased tensile strain of nanocomposites with increasing GO content are typical behaviour of a composite with enhanced strength and stiffness.⁴³ It is obvious from the results that GO can significantly improve the strength properties of epoxy. Improvement has been credited to (i) high elastic modulus and strength of GO, (ii) better interactions between graphene oxide and polymer matrix and; (iii) uniform dispersion of GO in the epoxy matrix due to abundant functional groups on the GO surface. Similar reinforcing improvement by GO-epoxy nanocomposites has been previously reported.^{11, 13-14, 44} GO contains oxygen containing functional groups across the surfaces which can form covalent bonds with epoxy matrix. Further, distortion caused by oxygen functionalization and extremely small thickness of GO sheets may lead to a wrinkled and rough surface of GO. Together with the wrinkled surface structure of GO which can enhance the mechanical interlocking with the polymer, the surface chemical reactions leads to stronger interfacial interactions and adhesion, and consequently results in efficient load transfer between the GO and the epoxy matrix.^{4, 9}

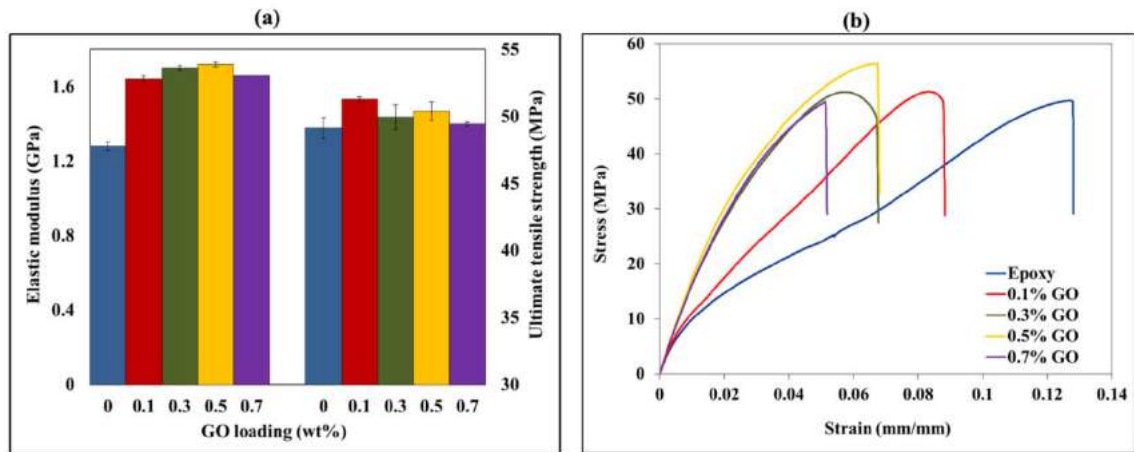


Figure 3.10. (a) Elastic modulus and tensile strength, and (b) tensile stress vs tensile strain curves of graphene oxide-epoxy nanocomposites.

Glass transition temperature (T_g) and curing behaviour

Glass transition temperature (T_g) of epoxy and its nanocomposites are shown in **Table 3.1**. T_g of pure epoxy is approximately 75.6°C. The T_g of neat epoxy was found to decrease slightly when GO was added to the resin and there was ~4°C decrease in the T_g with the addition of 0.7 wt% GO. Generally, the T_g of composites depends on the balance of two effects, influence on reaction conversion and molecular confinement. Graphene oxide is stiffer than epoxy matrix which could lead to significant confinement on the polymer chains.⁴⁵ On the other hand, GO may impede the epoxy curing reaction. This hindrance could be either because of chemical reaction of oxygen-containing functional groups of GO with curing agent (TETA) and/or epoxy resin or covering of reactive sites in the resin and the curative by graphene oxide sheets due to its high surface area. As a result, the optimized ratio of epoxy and curing agent in curing reaction was impacted. This would be expected to reduce the polymer cross-link density and so increase polymer chain mobility. Based on our result, it can suggest that the dominant effect of GO is obstruction of the epoxy curing reaction rather than molecular confinement, leading to positive effect on molecular chain mobility. The less restriction on molecular chain mobility grounds to decrease the T_g .^{14, 46}

Table 3.1. Glass transition temperature T_g of neat epoxy and nanocomposites.

Wt% of GO in epoxy	Glass transition temperature, T_g (°C)
0	75.6
0.1	73.0
0.3	71.5
0.5	68.7
0.7	71.5

The dynamic DSC heat flow curves of the neat epoxy and GO/epoxy systems are illustrated in **Figure 3.11**. The heat of cure (ΔH) in the GO/epoxy nanocomposite is significantly smaller than that of neat epoxy. The ΔH value decreased from 137.1 J/g of neat epoxy to 117.3 J/g of graphene oxide/epoxy nanocomposite with addition of only 0.3% GO. This immediately suggests that GO retarded the cure reaction of epoxy. However, the peak heat flow (T_p), i.e., the temperature of maximum heat flow during the cure reaction, remained unaffected. We have calculated the extent of conversion of the cure reaction (α) as a function of initial curing time using the heat flow curves and **Figure 3.11 (b)** shows the calculated data for neat epoxy and epoxy nanocomposite at 0.3 wt% GO. It can be observed that α of GO /epoxy systems in all time intervals are lower than those of neat epoxy. This suggests that curing reaction of baseline epoxy was slowed down with incorporation of GO into the epoxy matrix. These results further confirmed that GO acts as an obstacle in the curing reaction of epoxy. Retardant effect of GO could arise due to the reaction of oxygen functional groups of GO with amine groups in curing agent resulting in slowing of epoxy curing. The effects of graphene or its derivatives on curing of different epoxy systems have previously been reported. Qui *et al.*¹⁶ reported that GO has an accelerating effects on the curing process of TGDDM/DDS epoxy system. They observed that the oxygen functional groups on the surface of GO acted as catalysts and facilitated the curing reaction and the catalytic effect increased with the GO content. Bortz *et al.*¹³ reported similar effect of GO on DGEBA cured with 1, 2-diaminocyclohexane. They observed that the total heat of reaction increased with addition of GO. This effect though appeared saturated at 0.25 wt% GO. Nevertheless, the T_p remained unchanged. The acceleration effect has been explained by an increase of oxygen functional groups which could produce a catalytic effect on

epoxide ring opening, resulting in higher reaction rates. Teng *et al.*¹⁷ have observed steric hindrance effect of graphene on epoxy curing reaction. However, Park and Kim¹⁸ reported that graphene acted as a catalyst to speed up the epoxy curing rate.

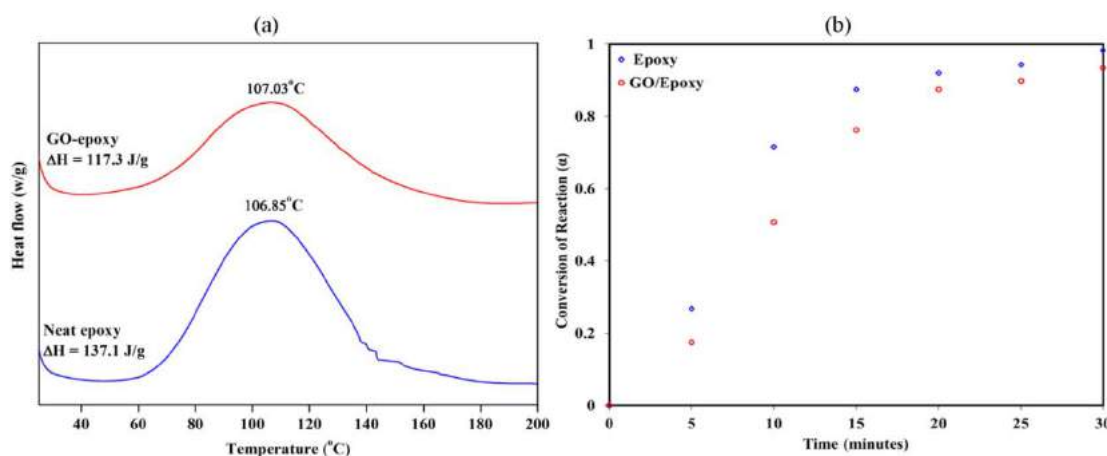


Figure 3.11. (a) DSC curves of neat epoxy and graphene oxide/epoxy nanocomposite at partially cure time of 0 (b) Conversion of reaction (α) as a function of partially curing time for neat epoxy and epoxy nanocomposite at graphene oxide loading of 0.3 wt%.

3.6 Conclusions

Bulk quantity of GO was prepared by chemical oxidation using modified Hummers method. Results showed that graphite could be completely oxidized to GO which is readily soluble in water and organic solvents. The incorporation of very low amount of GO into epoxy matrix has significantly enhanced mechanical performance of epoxy. The mode I fracture toughness increased up to 50% over neat epoxy with 0.1 wt% GO. Elastic modulus showed a steady increase with addition of GO from 0.1 to 0.5 wt% whereas there was no significant effect of GO incorporation on tensile strength. Improvement can be attributed to the superior properties of GO which include their high specific surface area, enhanced interaction/adhesion arising from their oxygen functional groups and wrinkled and rough surface and two-dimensional planar geometry. However, glass transition temperature decreased slightly with increasing GO content in the nanocomposites. Further, the total heat of cure of neat epoxy system is significantly larger than epoxy/GO nanocomposite. This result revealed that GO might retard the cure reaction of epoxy matrix. Retardant effect can cause to reduce the formation of crosslink in the matrix resulting in lower T_g of nanocomposite.

3.7 Acknowledgement

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3.9 Addendum to the chapter

Fracture toughness (K_{Ic})

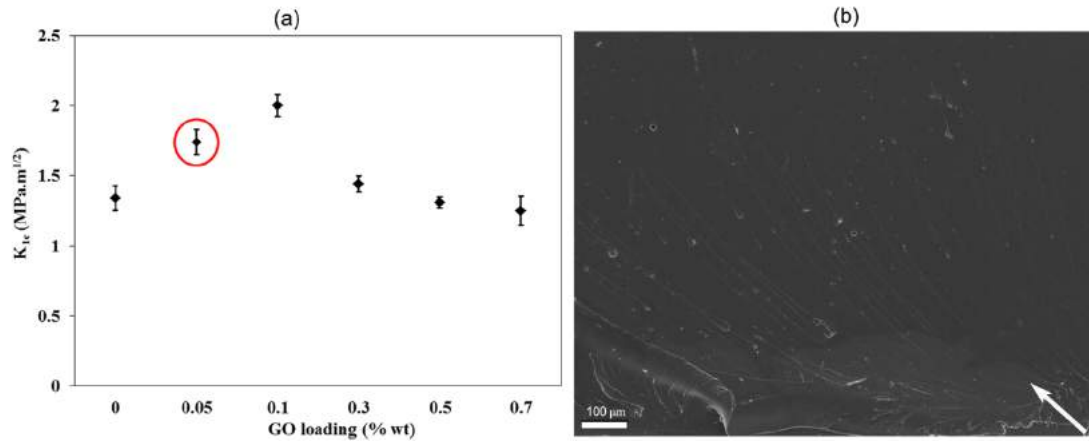


Figure 3.12. (a) Edited version of Figure 3.8 with additional data point of 0.05 wt% GO. (b) SEM of fracture surface of 0.05 wt% GO-epoxy nanocomposite.

Tensile properties

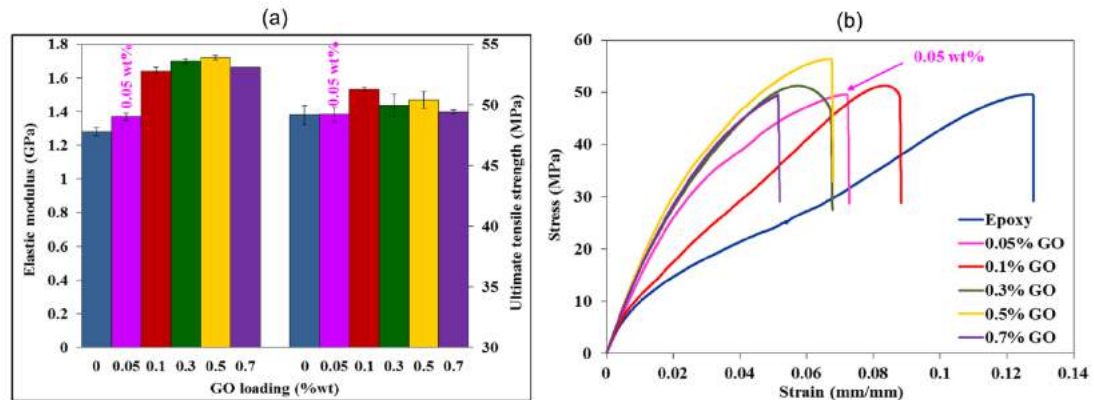


Figure 3.13. Edited version of Figure 3.10 showing elastic modulus, ultimate tensile strength and the tensile stress-strain curve with extra data point at 0.05 wt% GO.

After publication of this paper, we further characterized the nanocomposite containing 0.05 wt% GO in epoxy matrix to ensure optimal loading of GO to achieve better mechanical property. As shown in **Figure 3.12**, it is clear that 0.1 wt% GO can effectively enhance the fracture toughness by ~50 % compared to ~ 30% with 0.05 wt% GO. **Figure 3.13** shows the slight increase in elastic modulus with 0.05 wt% GO, whereas there is no noticeable effect on ultimate tensile strength. For the trace shown there is a disproportionate enhancement of the modulus from this sample compared to the epoxy and 0.1 wt % GO samples that merits further investigation. In

relation to fracture toughness the extra data confirmed the best GO loading for the significant enhancement in epoxy matrix is 0.1 wt%.

4 The Effect of Graphene Oxide and its Oxidized Debris on the Cure Chemistry and Interphase Structure of Epoxy Nanocomposites

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4.1 Prelude

Epoxy resins are thermosetting materials possessing high stiffness, dimensional stability and chemical resistance. Understanding the curing behaviour of epoxy systems is essential because improvement in the properties of the epoxy composites depends on the formation of the cross-linked molecular network in the system and the structure of the interphase region between the continuous phase (resin) and the discontinuous phase (reinforcement). The interphase region plays a critical role in determining those properties of the composites that depend on the interfacial load transfer between resin and nanofiller.

The effect of carbon fillers on amine curing processes and reaction mechanisms of several epoxy resin systems have been investigated using different techniques such as DSC, DMA, Raman spectroscopy etc. DSC is the most widely used of these techniques due to its simplicity but the technique does not generally provide chemical information and detailed mechanism of the cure process and in particular the chemistry of the interphase region between resin and reinforcement. Furthermore, we have seen that there has been significant inconsistency amongst reported results on effect of graphene or GO on the cure and its chemical mechanisms of epoxy.

In this paper, we investigate the influence of GO and OD (oxidative debris) on epoxy cure using FT-IES technique, which offers an analytical approach for *in situ* monitoring of the chemical reactions and mechanisms throughout the curing process. We observed that GO has significantly influenced the cure reaction and mechanism of epoxy which details in the paper.

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4.2 Statement of Contribution

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of the journals or other publications and (c) the head of the responsible academic unit, and
5. they agree to the use of publication in the student's thesis and its publication on the Australia Thesis Database consistent with any limitation set by publisher requirements.

In the case of this chapter:

The Effect of Graphene Oxide and its Oxidized Debris on the Cure Chemistry and Interphase Structure of Epoxy Nanocomposites

Accepted by Polymer with minor corrections

Contributor	Statement of contribution
Dilini Galpaya	Fabrication and characterization of graphene oxide and its nanocomposites, data analysis, paper writing
Joseph Fernando	UV study of graphene oxide, data analysis, Paper writing
Llew Rintoul	IES studies, paper writing
Nunzio Motta	paper writing
Eric Waclawik	paper writing
Cheng Yan	Overall supervision of the project, paper writing
Graeme George	Overall supervision of the project , paper writing

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Cheng Yan



16/6/15

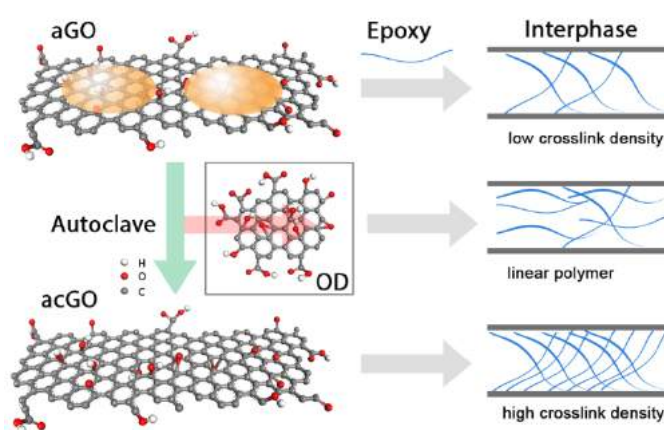
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Abstract

The influence of graphene oxide (GO) and its surface oxidized debris (OD) on the cure chemistry of an amine cured epoxy resin has been investigated by Fourier Transform Infrared Emission Spectroscopy (FT-IES) and Differential Scanning Calorimetry (DSC). Spectral analysis of IR radiation emitted at the cure temperature from thin films of diglycidyl ether of bisphenol A epoxy resin (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) curing agent with and without GO allowed the cure kinetics of the interphase between the bulk resin and GO to be monitored in real time, by measuring both the consumption of primary (1°) amine and epoxy groups, formation of ether groups as well as computing the profiles for formation of secondary (2°) and tertiary (3°) amines. OD was isolated from as-produced GO (aGO) by a simple autoclave method to give OD-free autoclaved GO (acGO). It has been found that the presence of OD on the GO greatly influences the associated cure kinetics mainly by preventing catalytic and active sites on GO surfaces from being reacted with DDM, which results in a lower crosslink density of the three-dimensional networks in the aGO-resin interphase compared to the acGO-resin interphase. We also observed that OD itself promoted homopolymerization. A DSC study further confirmed that the aGO nanocomposite exhibited lower T_g while acGO nanocomposite showed higher T_g compared to neat resin because of the difference in crosslink densities of the matrix around the different GOs.



Key words: Epoxy resin, Graphene oxide, Oxidative debris, Cure kinetics, Interphase, Nanocomposites

4.3 Introduction

Graphene oxide (GO) is a graphene derivative containing covalently attached oxygen-containing surface groups such as hydroxyls, carbonyl, carboxyl and epoxy groups. In general, it is accepted that hydroxyl and epoxy groups are bonded to the surface of graphene sheets and carboxyl groups are bound to the edges of the basal planes.¹ These functional groups can facilitate better exfoliation and dispersion in solvents and further surface functionalization.¹ Importantly, GO has an ideal surface for interacting with polymer matrices and several polymer nanocomposites with significantly improved mechanical properties have been developed.²⁻⁶ However, it has been recently reported that as-produced GO (aGO) is a mixture, containing lightly oxidized graphene sheets and heavily oxidised low molecular weight material. This oxidised low molecular weight material, called oxidative debris (OD) resembles the complex aromatic fulvic acid that is strongly bonded to aGO surface but can be removed by washing with alkaline solutions.⁷ The majority of the oxygen-containing groups found in bulk aGO are actually in OD and it is considered responsible for the observed excellent suspension in aqueous solutions as well as the fluorescence of graphene oxide.⁷⁻⁸ Further, some studies reported that OD is accountable for some inherent properties of bulk GO such as electroactivity.⁹

Epoxy resins are thermosetting materials possessing high stiffness, dimensional stability and chemical resistance.¹⁰ Understanding the curing behaviour of epoxy systems is essential because the thermal and mechanical properties of the epoxy composites depends on the formation of the cross-linked molecular network in the system and the structure of the interphase region between the continuous phase (resin) and the discontinuous phase (reinforcement). The interphase region plays a critical role in determining those properties of the composites that depend on the interfacial load transfer between resin and nanofiller. It has been shown that the dimensions of the interphase in carbon-fiber epoxy composites is 118 nm¹¹ so that a simple calculation shows that if the GO is fully exfoliated with a (hypothetical) surface area of 2630 m²/g, 100% of the resin is potentially in the GO interphase region at loadings as low as 0.5wt%. Mc Allister et al.¹² in their detailed study of the expansion and exfoliation of graphite oxide to produce single-sheet GO have noted that the real surface area reduces to values of 1850m²/g when suspended in solution (determined by methylene blue adsorption) and 600-900 m²/g in the solid state due to

aggregation (as measured by the BET isotherm). These values will be even further reduced if the GO is only partially exfoliated since it has been noted for expanded graphite oxide the surface area is $<100\text{m}^2/\text{g}$. In an epoxy resin-GO nanocomposite the effective interphase volume will depend on the method of sample preparation since exfoliation is a pre-cursor to interpenetration of the GO by the resin-hardener mix. Solution preparation involving ultrasonication¹³⁻¹⁴ is the simplest way to achieve this. A feature of these epoxy-GO nanocomposites is that very low loadings only are required to achieve significant changes in properties, including fracture toughness^{6, 15-19} which implies that the structure of the interphase may be responsible for these changes. Putz et al.²⁰ have noted that the high surface area means that the interphase may percolate the entire volume of the nanocomposite, so dominating the usual bulk properties such as glass transition temperature (T_g).

The final properties of the cured bulk resin are also determined by the chemical structure of both the resin and the curing agent. Epoxy resins contain at least two terminal epoxide groups which can be cured by various types of curing agents such as diamines, anhydrides or isocyanates.²¹ Amine curing process of epoxy generally involves three major reactions ie; 1° amine-epoxy, 2° amine-epoxy and hydroxyl-epoxy addition reactions as schematically shown in **Figure 4.1**.²²⁻²³

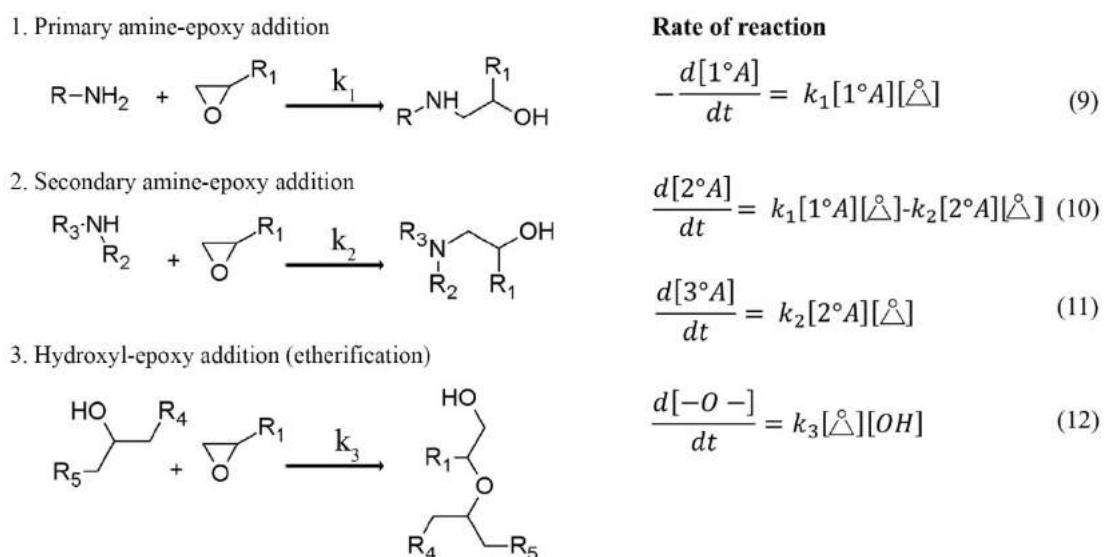


Figure 4.1. Schematic representation of three major reactions during the amine curing of epoxy resin and empirical equations for the rate of these reactions. Note that there are two epoxide and two 1° amine groups per molecule in the DGEBA-DDM system (see Figure 4.2).

The amine curing processes and reaction mechanisms of several epoxy resin systems have been widely investigated by means of differential scanning calorimetry (DSC)^{10, 15, 24}, dynamic mechanical analysis (DMA)²⁵, raman spectroscopy²⁶⁻²⁷, near-infrared (NIR) spectroscopy²⁸, infrared emission spectroscopy (IES)²², etc. DSC is the most widely used of these techniques due to its simplicity but it cannot provide explicit information on the chemical reactions during cure.²⁹⁻³⁰ Analysis provides information including cure enthalpy (ΔH_{cure}), glass transition temperature (T_g), reaction exotherm (onset temperature: T_{onset} , peak temperature: T_p) and (with some assumptions) activation energy (E_a). Several research studies reported that curing reaction in epoxy matrix can be influenced by the addition of filler materials. It has been noticed that metal oxides such as zinc, aluminium and iron oxides exhibit a catalytic effect on the epoxy curing consistent with adsorption of curing agent on to the metal particle surfaces.³¹⁻³² Moreover, interfacial effect of nanoparticles is generally higher than with micron-sized filler particles due to the much higher surface area of nanoparticles. The functional groups on the surface of GO are able to both react with the components of the epoxy resin and potentially catalyse the cure reactions. XPS and IR spectroscopy have identified oxirane, carboxylic acid and alcohol groups on GO surface.¹

As seen in **Table 4.1**, several studies focused on the effect of graphene materials on the cure behaviour of epoxy resins. It is clear from the table that all these studies have been carried out based on DSC technique. Nevertheless, it can be seen that there are discrepancies in outcomes among different research groups. Similarly, both accelerating and retardation effect of carbon nanotubes (CNTs) on different epoxy systems have been reported.^{24, 33-35} The disparity in results suggests that the epoxy-GO; epoxy-graphene or epoxy-CNT reactions are sensitive to the detailed chemistry of the epoxy resin system (especially the nature of the curing agent) as well as the functional groups on the surface of the carbon nanoparticles. A rationalization of these contradictory results may possibly be found in the work of Putz et al.²⁰ on carbon nanotube-epoxy composites. They found that two opposing effects may be seen: network disruption at the nanotube-polymer interface lowering T_g and formation of an interphase in which chain dynamics were retarded leading to a higher T_g . However, the conflicts may reflect the limitations of the DSC technique itself.

Table 4.1. Comparison of previously reported work on effect of graphene/GO on amine-epoxy curing.

Graphene derivative	Technique	Findings	Reference
GO	Non-isothermal DSC (Kissinger-Friedman analysis)	• Retardation effect	Ryu et al. ¹⁰
GO-amine modified		• Acceleration effect • Neutralization of NH ₂ by COOH-GO	
GO	DSC (ΔH , T_p , T_{onset})	• Acceleration effect • Catalytic effect on epoxy ring opening reaction by 'O' groups on GO	Bortz et al. ¹⁵
GO	Non-isothermal DSC	• Acceleration effect	Qui et al. ³⁶
Graphene/GO	DSC (T_g)	• Catalytic effect on both 1° and 2° amine-epoxy reactions	Mauro et al. ³⁷
Graphene	DSC (ΔH , T_p)	• Retardation effect • Steric hindrance	Teng et al. ³⁸
Graphene	DSC (T_g)	• Catalytic effect • Catalytic effect of OH on epoxy-amine reaction	Park et al. ¹⁷

Although the kinetics of cure reaction has been widely studied by DSC, the technique does not generally provide chemical information and detailed mechanism of the cure process and in particular the chemistry of the interphase region between resin and reinforcement.³⁹ One of the major limitations of DSC is that it is a bulk measurement and if the graphene or GO sheets are not fully exfoliated then changes in the heat flow due to reaction of the functional groups in the interphase with the bulk epoxy resin and curing agent are going to be small. If the system is exfoliated and has a high surface area then DSC is a useful method for studying changes in cure exotherm and T_g , but an assumed order of reaction is required to generate kinetic data with non-isothermal studies at different heating rates being particularly problematic. Isothermal studies are therefore preferred when cure reactions are studied.

The FT-IES method described here offers an alternative analytical approach to monitor the chemical reactions and mechanisms throughout the curing process. Emission of infrared radiation occurs from all bodies at ambient temperature and may be imaged with IR cameras, but in most cases the spectral information is lost due to reabsorption of the radiation and temperature gradients within the body. When the emitter is a thin film, reabsorption and temperature gradients are minimized and IR emission spectra equivalent to IR absorption may be obtained.²² The emission intensity is weak at room temperature due to the low population of the higher vibrational states, but at the cure temperatures of many resin-hardener systems ($\geq 100^\circ\text{C}$) there is a significant intensity in the “fingerprint” region of the IR spectrum so that the cure chemistry may be followed in real time.

Use of the technique on very thin film samples gives an added advantage of offering the information on the interphase region where molecular chemical reactions occur during the curing process. Because of the specialized nature of the technique, limited investigation of amine curing of epoxy resin based on IR emission has been reported. George et al.²² reported a detailed kinetic study on the curing of TGDDM/DDS epoxy mixture transferred as a thin film from the surface of carbon fibre-epoxy prepregs. They observed the spectral changes during cure which were used to monitor the chemical changes and to study the cure kinetics. For example; decrease in both the 1° amine bending band at 1652 cm^{-1} and epoxy cyclic ether band at 906 cm^{-1} and increase and broadening of ether group at 1085 to 1140 cm^{-1} and hydroxyl group at 1000 to 1100 cm^{-1} were observed with the progress of cure. These observations are consistent with the sequence of reactions occurring during the cure (**Figure 4.1**). Calculated activation energies (from Arrhenius plots) showed that homopolymerization is dominant in catalysed resin from epoxy prepregs compared to a model system where auto-catalysed 1° amine-epoxy reaction is favoured.

In this article, we wish to evaluate the influence of GO on the curing process and also to understand the chemical reaction mechanisms at the interphase of epoxy resin and GO during the curing process based on the FT-IES method. We further study the effect of OD on cure kinetics of epoxy. DSC studies were also conducted in parallel with the IR emission experiments for an independent measure of extent of reaction with time of cure and also the T_g of the system at different extents of reaction. We

believe that this opens up a new approach to evaluate and understand curing behaviour and structure of epoxy nanocomposites, especially at the interphase.

4.4 Experimental

The materials used in this study were the commercial DGEBA resin (Diglycidyl ether of bisphenol A) epoxy resin (DGEBA) and curing agent DDM (4, 4'-diamino-diphenylmethane). Typical structures of DGEBA and DDM are presented in **Figure 4.2**.

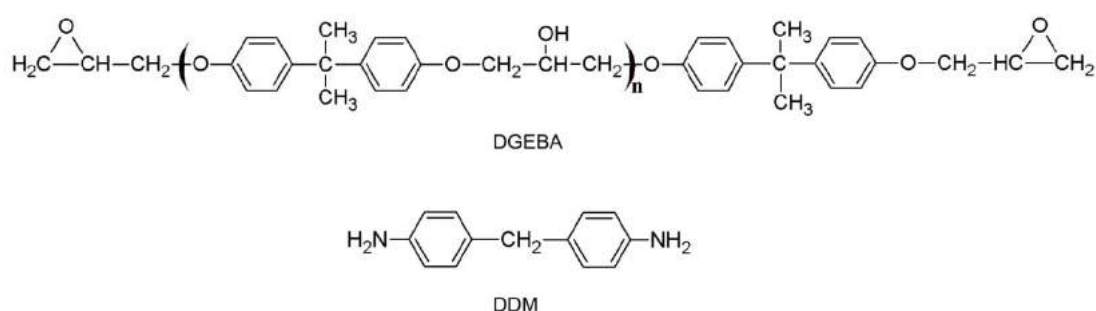


Figure 4.2. Schematic of DGEBA (n=0.1) and DDM structures.

GO was prepared, following a modified Hummers method (supporting information).⁴⁰ As produced GO (aGO) was purified and OD was isolated by an autoclave method which avoided the complications of base washing. Autoclaved GO is called acGO hereafter. More details on synthesis and characterization of aGO, acGO and OD can be found in supporting information for this paper. aGO, acGO and OD were characterized by different microscopic methods such as SEM, TEM, AFM and spectroscopic methods; FTIR, Raman, XPS (see supporting information). The surface area of the aGO was estimated by the Methylene blue (MB) method reported by Navajas et al.⁴¹ as detailed in supporting information.

4.4.1 IR emission study

To achieve thin films on the FT-IR emission hotplate, solutions of known concentration were deposited from dimethylformamide (DMF). The resin mixture was prepared by dissolving the required amounts of DGEBA and DDM (weight ratio of 2:1) in a small amount of DMF at room temperature. Resin mixture with GOs (aGO or acGO) was prepared by firstly exfoliating and suspending GO in the DMF (1mg/ml) by sonicating for 1 h and then adding the required amount of GO solution

into the resin mixture at room temperature. GO content used in this study was 0.3 wt% in the total resin mixture which was chosen since it provides a homogeneous dispersion and most of previous work reported that the maximum property enhancement was achieved with a graphene or GO loading of 0.1 – 0.5 wt%.^{6, 15-16, 18-19, 42} In the case of OD, powdered OD isolated from the water after autoclave treatment of GO was dissolved in water and then added into DGEBA-DDM mixture in DMF. Water and DMF are completely miscible and gave a clear solution.

FT-IES emission analysis was performed with a Nicolet spectrometer equipped with a liquid N₂ cooled mercury cadmium telluride detector and an external graphite furnace emission accessory, described elsewhere.⁴³ The graphite furnace was fitted with either a platinum hotplate of 6 mm diameter or a graphite reference plate. 1 μ l of uncured epoxy mixture in DMF was transferred by a micro-syringe on to the platinum plate, pre-heated to 100°C to get a very thin film of the sample on the plate. The solvent evaporated immediately after putting the sample on the platinum plate so there was no solvent interference in the sample spectra. IR emission spectra were collected under dry air immediately the sample was deposited.²² The average spectrum of 128 scans was obtained at spectral resolution of 4 cm⁻¹. Successive single beam spectra were collected at every 2 minutes for an initial 16 minutes and then every 5 minutes for a total cure time of 30 minutes.

To linearise the spectra with respect to concentration, equivalent absorbance spectra were calculated by exploiting the relationship between absorbance and emittance, $A \approx -\log(1-\epsilon)$, where ϵ is the ratio of the sample signal to the graphite signal after accounting for the contribution of the clean Pt substrate and instrument background contributions. Spectra of different concentrations of DGEBA resin (10, 5, 2.5 and 1 mg/ml) were obtained to get the relationship between concentration and peak intensity.

4.4.2 DSC study

DSC study was conducted with a TA instruments Q100 differential scanning calorimetry. Samples were prepared following the similar procedure as described above using acetone as the solvent. This is because the lower boiling point of acetone facilitates the faster evaporation of the solvent at lower temperature, so avoiding premature cure of the resin-hardener mixture. Acetone was evaporated by stirring the epoxy resin at 40°C for few hours on a hot plate with a magnetic stirrer. Then the

hardener was mixed and the mixture was placed under vacuum at the same temperature for further 1 hour for the complete removal of solvent. A series of DSC samples were prepared by adding ~5 mg into the hermetic type DSC aluminium pans which were thermally equilibrated in an oven at 100°C. Each sample was partially cured by removing them from the oven at different time intervals (0, 5, 10, 15, 20, 25 and 30 minutes). The heated samples were immediately put in the deep-freezer to stop the reaction. Then, the heat flow curves were obtained for each sample at a scanning rate of 10°C/min from 20 to 200°C under nitrogen atmosphere. The total heat of reaction (ΔH) was calculated using the heat flow curves and the conversion of the cure reaction (α) was determined at each time, t , as $\left(1 - \frac{\Delta H_t}{\Delta H_o}\right)$.

4.5 Results and discussion

aGO, acGO and OD prepared in this study were characterized by several spectroscopic and microscopic techniques prior to fabricating the nanocomposites. The atomic compositions of GOs were obtained from the XPS analysis and revealed that aGO contains 66.6 atom% of Carbon and ~30.4 atom% of Oxygen. The oxygen content decreased to ~ 14 atom% and C increased up to ~ 85 atom% in acGO after autoclave treatment (supporting information- **Figure 4.14**). This confirms the removal of oxygen functional groups during the autoclave cleaning process. XRD data further confirmed the change of interlayer distance of aGO after autoclave process. Estimated surface area of aGO is 719 m²/g as determined by methylene blue binding (supporting information) which is comparable to values reported in literature.^{12, 41}

4.5.1 IR emission study

The raw emission spectra, all collected at 100°C, necessary to determine the equivalent absorbance spectrum of DGEBA-DDM are shown in the **Figure 4.3**.

These are, from top to bottom:

1. A graphite black body
2. A thin film of uncured DGEBA-DDM on the platinum hotplate
3. The clean platinum hotplate

The lowest (green) curve in **Figure 4.3** represents the emission spectrum of DGEBA-DDM at 0 min cure, shown in calculated absorbance units.

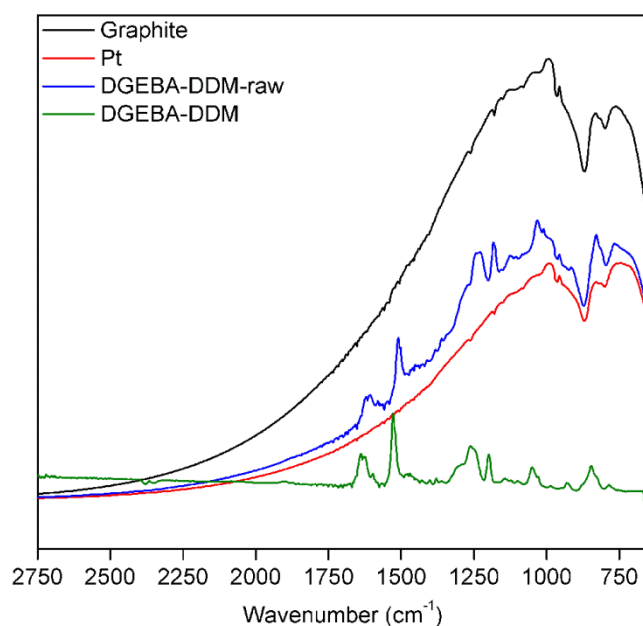


Figure 4.3. IR emission spectra at 100°C of (from the top): graphite reference plate; the DGEBA-DDM sample on the platinum plate; the clean platinum plate and the equivalent absorbance spectrum of the sample, calculated from these curves.

As an illustration of the quantitative aspects of the FT-IES analysis, different layers have been deposited of DGEBA resin without curing agent but at different concentrations in DMF. In each case 1 μ l of solution was deposited and as shown in **Figure 4.4**, the peak heights scale as expected for films of thickness corresponding to 0.5, 0.25, 0.1 times the original thickness. Further, this also indicates that the calculated absorbance scale is quantitative with respect to concentration so can be used for kinetic studies of cure. The calculated thicknesses range from 1150 nm to 115 nm which illustrates the sensitivity of the technique for studying the cure chemistry of the interphase with even partial exfoliation. It should be noted that in some runs there are unavoidable traces of water vapour in the sample compartment that result in underlying bands that may appear positive or negative after ratioing to the platinum reference spectrum in the region from 1800 cm^{-1} to 1500 cm^{-1} . These do not affect the quantitative analysis of the resin components.

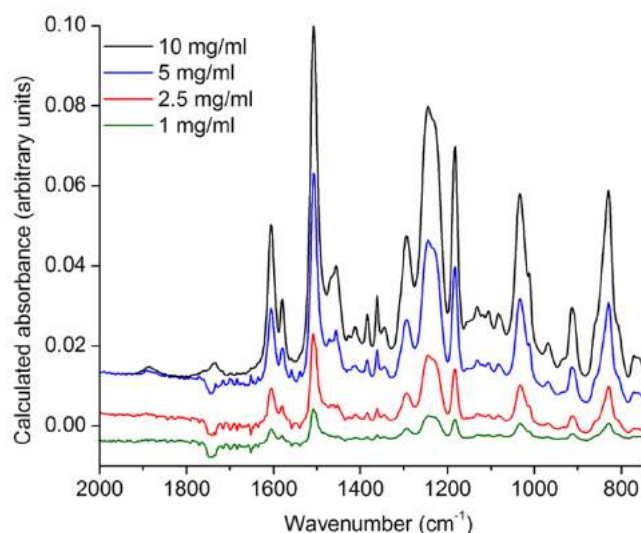


Figure 4.4. FT-IR emission spectra of thin films of DGEBA at 100 °C after deposition of 1 µl of DMF solution of concentration (from top to bottom curves); 10 mg/ml; 5 mg/ml; 2.5 mg/ml and 1 mg/ml.

IR emission spectra of DDM, DGEBA and DGEBA-DDM are shown in **Figure 4.5** and the functional group and reference bands that have been used for the cure study are tabulated in **Table 4.2**.

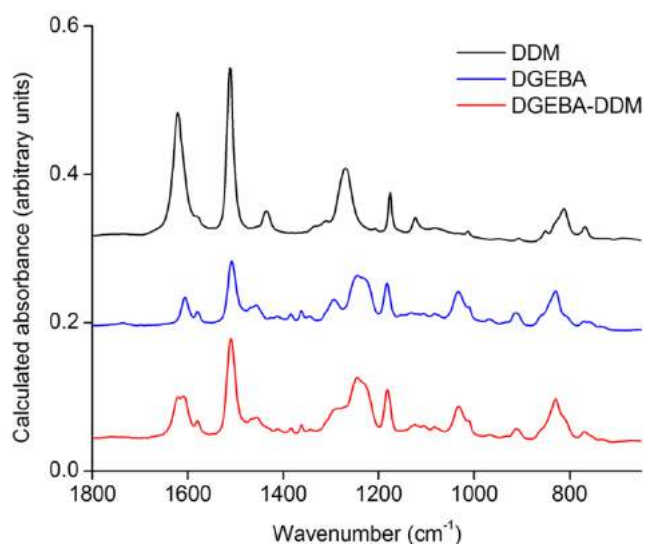


Figure 4.5. IR emission spectra (from top to bottom curves) of DDM, DGEBA and DGEBA-DDM (at the weight ratio of 2:1) at 100°C.

Table 4.2. List of functional and reference bands (used to normalize functional bands) of the DGEBA-DDM system used for the cure study.

Functional band	Wavenumber (cm^{-1})	Reference band (Used for Normalization)	Wavenumber (cm^{-1})
N-H bend (1° amine)	1621	C-H bend/ Benzene ring stretch	1511
N-H wag (1° & 2° amine)	768	C-H wag	1180
Epoxy ring stretch	914	C-H wag	1180
Ether	1100	C-H wag	1180

4.5.2 Emission spectral changes during cure of DGEBA-DDM

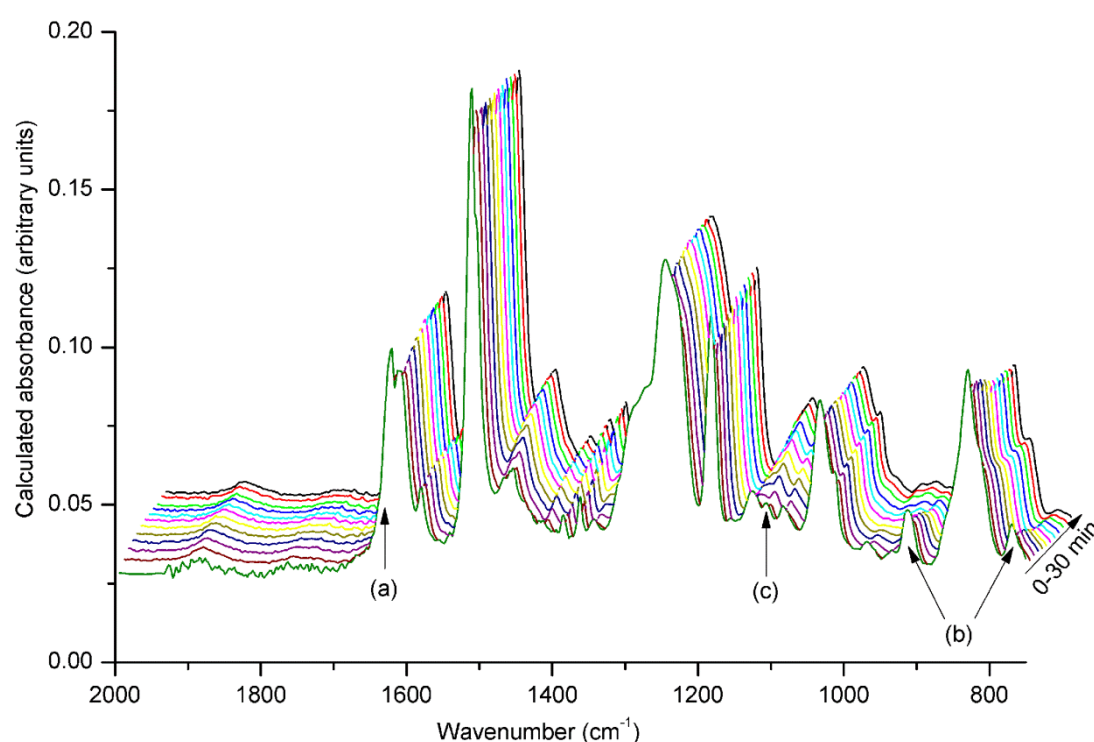
**Figure 4.6.** Stack plot of successive spectra of DGEBA-DDM at 100 °C for cure up to 30 minutes. The bands labelled (a), (b) and (c) are shown expanded in Figure 4.7.

Figure 4.6 shows a series of 12 successive spectra obtained continuously during the curing of neat epoxy resin at 100°C under dry air for 30 minutes. The spectrum at 0 min. represents the different functional groups of both epoxy resin and curing agent at the start of curing. The subsequent spectra show the emission curves at different stages of curing. The first spectrum is noisier in the region 2000 cm^{-1} to 1400 cm^{-1} compared to rest of the spectra. This is due to the effect of atmospheric moisture which may flow into the testing chamber on opening of the chamber for

sample insertion. The moisture effect disappeared in the following spectra with continued flushing of dry air into the chamber. The spectral changes during the curing can be clearly seen from the stacked spectra.

The sharp peak (a) at 1621 cm^{-1} is due to NH bending of the 1° amine band of DDM. This peak decreased rapidly with heating as it can be seen in the expansion plots of spectra in **Figure 4.7 (a)**. Similarly, epoxy peak at 914 cm^{-1} and NH wag band at 768 cm^{-1} diminished significantly with the progress of curing (**Figure 4.7b**). Decrease of peak intensities indicates the consumption of the amine and epoxy functional groups to form the 3D network structure during the curing process but more detailed analysis is required to separate the individual reactions 1 to 3 in **Figure 4.1**. Further, we observed the increase and broadening of peak at around 1100 cm^{-1} (**Figure 4.7c**) which is consistent with the formation of ether groups by etherification reaction between hydroxyl and epoxy (**Figure 4.1**, reaction 3) and homopolymerization. **Table 4.2** shows the peaks that change during cure and the band assignments. Similar spectral changes during the amine curing of epoxy systems have been reported in literature.^{22, 44}

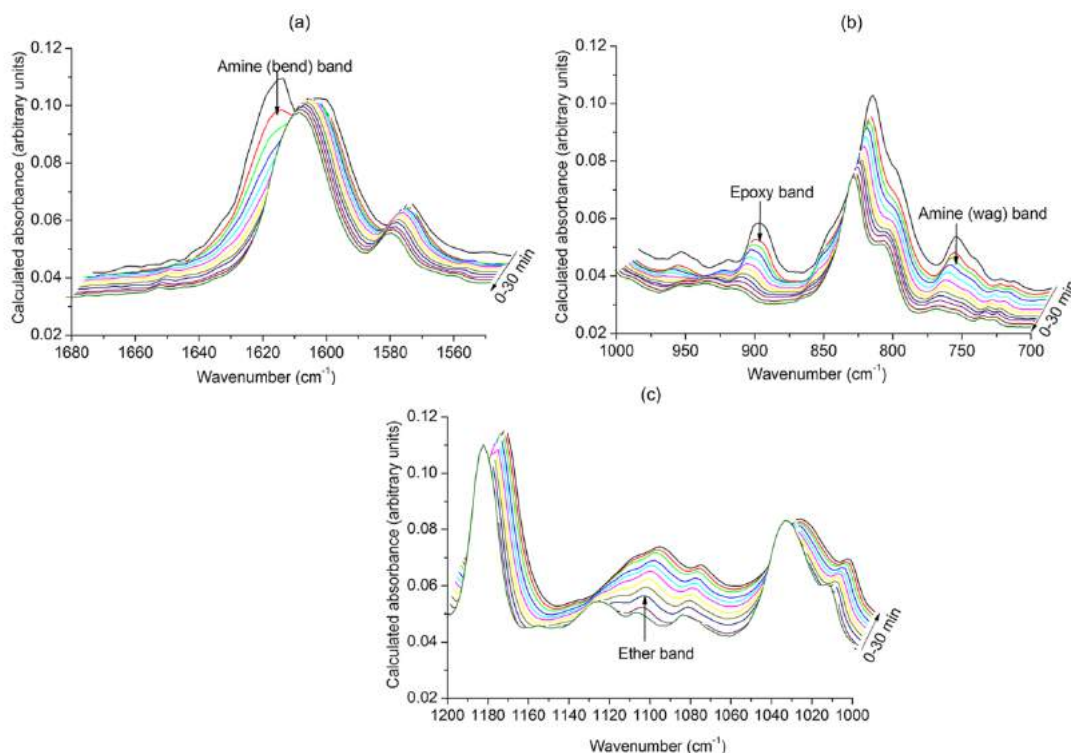


Figure 4.7. Expanded and reoriented stack plot of successive spectra of Fig 6., showing (a) consumption of 1° amine as change of N-H bend band (b) consumption of epoxy and N-H wag of 1° and 2° amine band (c) growth of ether band.

To investigate the influence on epoxy resin cure chemistry of as-prepared and autoclaved GOs (aGO and acGO, respectively) and the OD obtained after autoclaving, the cure kinetics of DGEBA-DDM nanocomposites were studied using the same experimental conditions at GOs or OD loading of 0.3wt%. Similar spectra and spectral changes were observed as shown in the supporting information, **Figure 4.19**, but it was apparent that the rates of the reactions of the species responsible for the spectra have changed when compared to the bulk resin. These changes are attributed to the influence of GOs on the detailed cure chemistry. Since the emission intensity bands when converted to absorbance are proportional to the concentration of the species, spectral manipulation allows the time-dependent concentration profiles of epoxide, 1° amine and 2° amine to be monitored with time of cure and instantaneous reaction rates determined.

4.5.3 Influence of GOs on the cure reactions of DGEBA-DDM from IR emission spectra

The cure kinetics and the effect of GOs and OD addition on the curing process were determined by analysis of the spectral changes in different nanocomposite systems. **Figures 4.8** and **4.9** display the change of band intensities due to the epoxy group from normalized spectral peak area at 914 cm^{-1} , amine groups determined by normalized spectral peak area at 1621 cm^{-1} (N-H bend) and 768 cm^{-1} (N-H wag) and the ether group from normalized spectral peak area at 1100 cm^{-1} in the epoxy resin and its nanocomposites. Peak normalization was done by dividing those bands with the reference bands given in **Table 4.1** at the same curing time. The band intensity changes arise from the chemical reactions shown in **Figure 4.1** and the instantaneous slopes of the lines in **Figures 4.8** and **4.9** reflect the rate of these reactions during cure. It is clear that 1° amine and epoxy groups gradually decrease in concentration during resin cure, due to epoxy-amine addition (**Figure 4.1**, reaction 1) which has been reported as the dominant reaction up to gelation.²²⁻²³

4.5.3.1 Epoxy consumption including etherification reaction

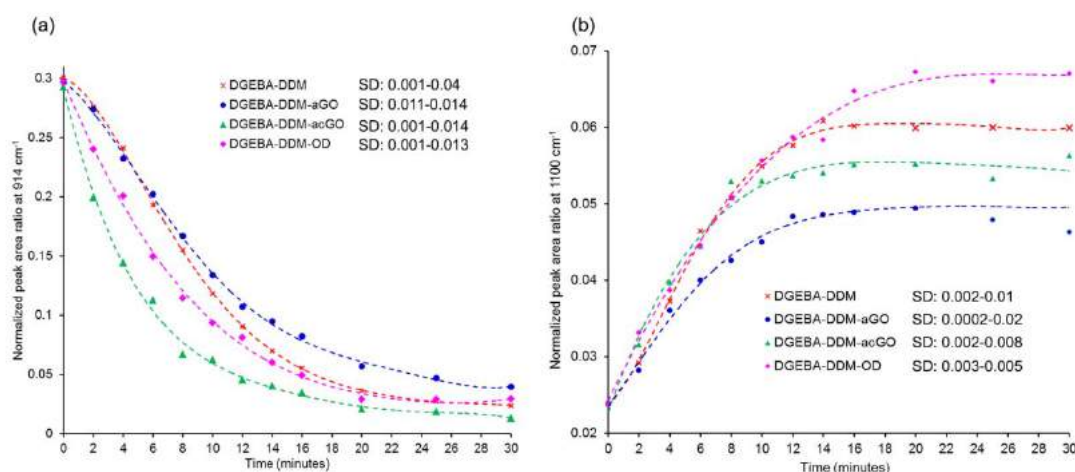


Figure 4.8. (a) Consumption rate of epoxy group at 914 cm⁻¹ and (b) formation rate of ether group at 1100 cm⁻¹ during cure at 100°C of DGEBA-DDM (-x-/red), DGEBA-DDM-aGO (-•-/blue), DGEBA-DDM-acGO (-▲-/green) and DGEBA-DDM-OD (-♦-/pink). All data were normalized with initial value of DGEBA-DDM for comparison. Dashed lines represent the trendline of the individual curves. SD values show standard deviation for each system.

The rate of epoxy consumption by the reactions with amine shown in **Figure 4.1**, reaction 1 to 3 is given by equation 13.

$$-\frac{d[\triangle]}{dt} = k_1[\triangle][1^\circ A] + k_2[\triangle][2^\circ A] + k_3[\triangle][3^\circ A] \quad (13)$$

It is important to note in **Figure 4.8 (a)** that compared to neat DGEBA-DDM, aGO-epoxy nanocomposite shows a slower rate of epoxy group consumption whereas acGO-epoxy and OD-epoxy systems exhibit faster rate of epoxy consumption. The consumption of epoxy is autocatalytic in both the neat DGEBA-DDM resin and the nanocomposite with aGO (as seen by the slower initial rate) but this is not seen from samples containing either OD or acGO. This suggests that both of these contain catalytic sites that enhance the ring-opening of the epoxy.

The rate of epoxy consumption with amine is given by equation 13. The initial epoxide consumption rates, $-d[\triangle]/dt_{(initial)}$, calculated from data before normalization are given in **Table 4.3** and are 0.037 Amin⁻¹ and 0.022 Amin⁻¹ for acGO nanocomposite and OD system respectively, where A is the peak area ratio in **Figure 4.8 (a)** which is proportional to epoxy concentration. These values may be

compared to 0.01 Amin^{-1} from the neat DGEBA-DDM system indicating that there is a clear change in reaction mechanism in the presence of acGO and OD.

Table 4.3. Initial rates of epoxy and 1°A amine consumption from FT-IES band areas.

System	$-\text{d}[\frac{\text{O}}{\triangle}]/\text{dt}_{(\text{initial})}$ Amin^{-1}	Rate, r, relative to DGEBA- DDM	$-\text{d}[1^\circ\text{A}]/\text{dt}_{\text{initial}}$ Amin^{-1}	Rate, r, relative to DGEBA- DDM
DGEBA-DDM	0.01	1.0	0.049	1.0
acGO	0.037	3.7	0.079	1.61
aGO	0.01	1.0	0.043	0.88
OD	0.022	2.2	0.029	0.59

As shown in **Figure 4.1**, during each epoxy ring-opening reaction, a hydroxyl group is formed. Another epoxide group may then react with this hydroxyl group (equation 12) to form an ether. A further epoxide reaction is homopolymerization which also creates ether linkages and is catalysed by tertiary amines or Lewis acids.^{22, 45} However, it is reported that in the absence of catalyst, hydroxyl-epoxide reaction or homopolymerization are less likely to occur at the early stage of curing.²² However, etherification is occurring as seen from the growth in the band at 1100cm^{-1} as plotted in **Figure 4.8 (b)**.

Etherification results (**Figure 4.8 (b)**) showed a faster reaction of acGO and a slower reaction of aGO nanocomposites compared to neat DGEBA-DDM resin. Importantly, the OD-system has a faster rate of formation and a higher concentration of ether groups than that of neat DGEBA-DDM resin which is consistent with the epoxy consumption rates being due in part to a higher extent of etherification in the presence of oxidized debris. Further support for etherification enhancement in OD systems is found later in the slower rate of epoxy-amine reaction compared to neat resin (**Table 4.3** and Section 4.5.3.2.) where the competing reactions are discussed in more detail.

4.5.3.2 1° amine - epoxy reaction

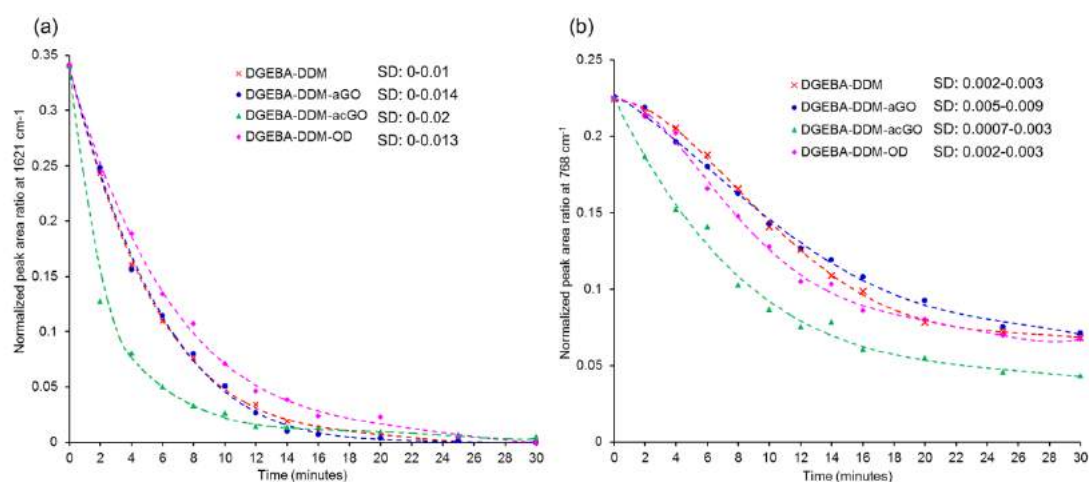


Figure 4.9. Consumption rate of (a) 1° amine (N-H bend) at 1621 cm⁻¹ (b) 1°/2° amines (N-H wag) at 768 cm⁻¹ during cure at 100 °C for 30 minutes of DGEBA-DDM (-x-/red), DGEBA-DDM-aGO (-•-/blue), DGEBA-DDM-acGO (-▲-/green) and DGEBA-DDM-OD (-♦-/pink) All data were normalized with initial value of DGEBA-DDM for comparison. Dash lines represent the trendline of the individual curves. SD values show standard deviation for each system.

The change in the normalized peak area of 1° amine N-H bending at 1621cm⁻¹ is similar for both neat epoxy resin and aGO nanocomposite throughout the curing process (**Figure 4.9 (a)**). In contrast, acGO nanocomposites show significantly faster decrease in 1621cm⁻¹ band while the OD system shows a slightly slower decrease compared to the neat DGEBA-DDM during cure. The initial rate of 1° amine consumption of DGEBA-DDM-aGO is very similar to that from DGEBA-DDM, so this suggests there is no contribution from reactive groups on the aGO such as surface epoxides. From the initial change of 1° amine from **Figure 4.9 (a)**, the initial rates (as $-d[1^\circ A]_{\text{initial}}/dt$) values can be calculated and are shown in **Table 4.3**. A is the normalized 1° amine band area from the FT-IES spectrum which is proportional to $[1^\circ A]$. An important result in **Table 4.3** is that the rate of reaction of 1° amine in the presence of OD is only 59% of that of the neat resin which suggests that it is the oxidative debris that is suppressing the reactivity of the aGO. The ratio of rates: $r_{\text{(acGO)}}/r_{\text{(aGO)}}$ is 1.84 which means that removal of OD increases the 1° amine consumption rate by 84% which may reflect the recovery of a catalytic effect of the “clean” surface of acGO on removal of OD. The catalysis is apparent since as shown in **Table 4.3**, $r_{\text{(acGO)}}/r_{\text{(DGEBA-DDM)}}$ is 1.61.

From **Table 4.3**, OD shows a faster initial rate of epoxy consumption compared to the neat DGEBA-DDM in spite of the slower rate of amine consumption noted above. This suggests that OD may induce the ring opening reaction of epoxide in the system i.e. homopolymerization is favoured. Proposed ring opening reaction and homopolymerization are schematically shown in **Figure 4.10**. It is believed that acGO is not favouring homopolymerization since there is faster consumption of 1° amine than aGO and also the 2° amine reaction is not suppressed to the extent that it is in aGO (**Figure 4.9 (b)**), which is discussed in more detail in Section 4.5.3.3.

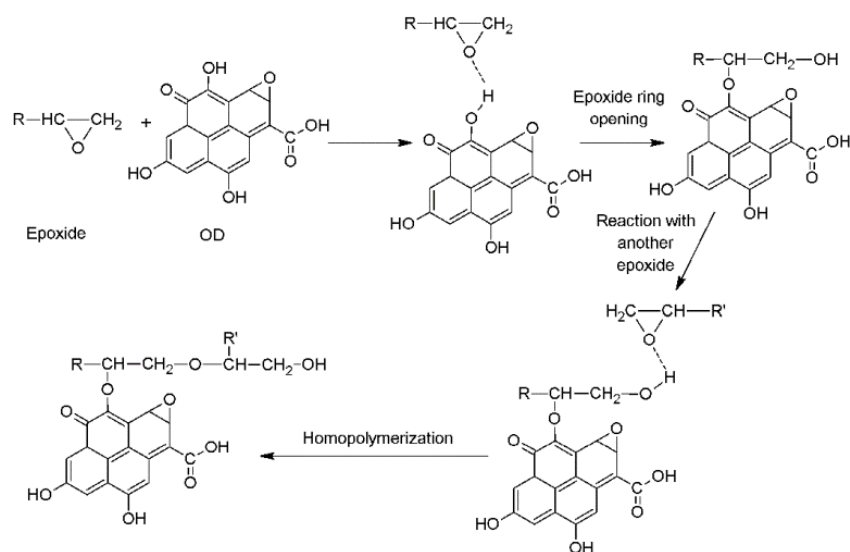


Figure 4.10. Schematic of effect of OD on epoxy homopolymerization.

OD represents about 14-30% of total mass of aGO and is strongly adhered to the graphene oxide surface.⁷⁻⁸ This adhered OD can physically cover the active sites (eg bound epoxide groups, hydroxyl groups, defects etc.) on GO surface which would act as reactants or catalysts of epoxide-amine reaction. Removal of OD exposed these active groups which can actively participate in catalysing epoxide-amine reactions or reacting directly with amines, resulting in faster epoxide-amine reaction and consequently, higher consumption of 1° amine. Mauro and co-workers performed a DSC-based investigation to elucidate the catalytic activity of graphene based nanofillers on epoxy curing reaction.³⁷ They observed that graphene or GO is able to catalyse the epoxide-amine reaction and catalytic effect can be on both reactions between 1° amine and epoxide as well as reactions between 2° amine and epoxide groups. It is also well known that graphene and GO have catalytic effects on several other organic reactions.⁴⁶⁻⁴⁸ In those studies the catalytic effect of base

washed (OD-free) GO on aerobic oxidative coupling of 1° amines was evaluated and compared with as-produced GO and OD.⁴⁸ Results showed that OD-free GO has significant catalytic activity with oxidative coupling product of 89% compared to lower catalytic effect of controlled aGO and OD samples (44% and <2% yield, respectively). The synergistic catalytic effect originates from combination of greater access to the catalytic sites by the reactants, exposed carboxylic acid groups and unpaired electrons at the edge defects with the removal of OD.⁴⁸

4.5.3.3 2° amine formation and reaction

As noted above in Section 4.5.3 and **Figure 4.7 (b)**, the peak at 768cm⁻¹ is due to N-H wag of both 1° and 2° amines.⁴⁵ The contributions of the concentration of the 1° amine to the band intensity (from the 1° amine bend band at 1621 cm⁻¹) may be subtracted and the change in concentration of 2° amine during cure determined from equation 14:

$$A_{\text{NH wag}} - aA_{\text{NH bend}} = b[2^\circ\text{A}] \quad (14)$$

Where;

$A_{\text{NH wag}}$ = Normalized peak area ratio of NH wag band

$A_{\text{NH bend}}$ = Normalized peak area ratio of NH bend band

$[2^\circ\text{A}]$ = Concentration of 2° amine

a, b = Constants related to the molar absorptivity of the bands analysed

a is determined from the spectrum at 0 minute. At 0 min, $[2^\circ\text{A}] = 0$, Therefore,

$$a = \frac{A_{\text{NH wag}}}{A_{\text{NH bend}}}$$

The calculated parameter $b[2^\circ\text{A}]$ has been plotted against the curing time for the 4 different systems in **Figure 4.11**. The formation of 2° amine occurs from the onset of cure due to the reaction of epoxide with 1° amine group and this concentration increased rapidly at early stages of curing (**Figure 4.1**, reaction 1). The 2° amines can further react with epoxide groups forming 3° amine (**Figure 4.1**, reaction 2) which results in formation of the 3D network structure in the resin matrix. Therefore there is a consecutive reaction of creation and consumption of 2° amine as seen by the growth to a maximum in **Figure 4.11**. Then, depending on the relative

magnitude of the rate coefficients for 2° and 3° amine formation this profile will change.

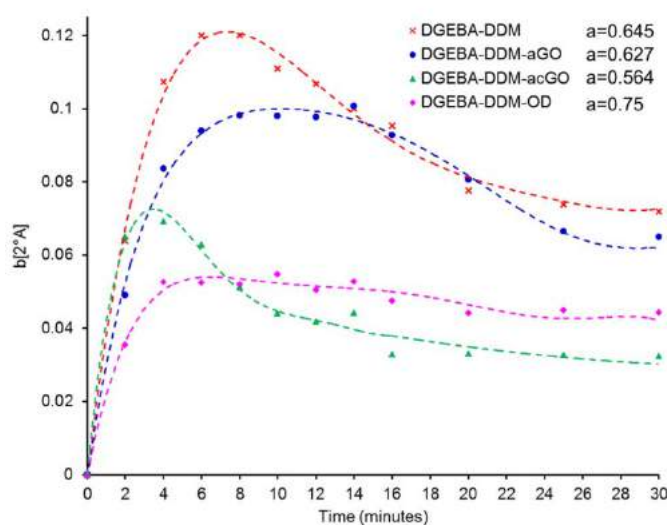


Figure 4.11. Calculated 2° amine concentration from emission spectra during the cure of DGEBA-DDM (-x-/red), DGEBA-DDM-aGO (-•-/blue), DGEBA-DDM-acGO (-▲-/green) and DGEBA-DDM-OD (-♦-/pink) at 100°C for 30 minutes. Dash lines represent the trendline of the individual curves. The calculated values for “a” for each system are shown in the plot.

For consecutive second order reactions, at the maximum [2°A] at time t , then

$$\frac{d[2^\circ A]}{dt} = 0$$

So, from **Figure 4.1**- equation 10, $k_1[1^\circ A][\triangle] = k_2[2^\circ A][\triangle]$

Hence, at this point:

$$\frac{k_1}{k_2} = \frac{[2^\circ A]_t}{[1^\circ A]_t} \quad (15)$$

and in principle the ratio of rate coefficients of 1° and 2° amine reaction with epoxide, k_1/k_2 , could be determined from the data in **Figures 4.9 (a)** and **4.11**. However, as may be seen from **Figure 4.11**, the plot is of $b[2^\circ A]$ against time so there is an unknown constant, b , due to the unknown molar absorptivity of the species being measured in the FT-IES spectra. In spite of this limitation it is possible to calculate the rate coefficient, k_2 , for each system relative to the neat epoxy resin in the way shown below to give an empirical value $k_{2(\text{rel})}$. **Table 4.4** shows the calculated ratios bk_1/k_2 for four systems from the data in **Figures 4.9 (a)** and **4.11** taken at the maxima of the curves in **Figure 4.11** together with the calculated $k_{2(\text{rel})}$

using these results plus the relative rate of 1° amine consumption compared to neat DGEBA-DDM in **Table 4.3**.

Table 4.4. Calculated ratio bk_1/k_2 and the rate coefficient $k_{2(\text{rel})}$ of 2° amine reaction in the system relative to that in neat DGEBA-DDM resin.

System	bk_1/k_2	$k_{2(\text{rel})}$
DGEBA-DDM	1.33	1.00
DGEBA-DDM-aGO	2.13	0.55
DGEBA-DDM-acGO	1.15	1.40
DGEBA-DDM-OD	1.21	0.49

A sample calculation of $k_{2(\text{rel})}$ is given below for the system DGEBA-DDM-aGO.

$$\frac{bk_{1(\text{DGEBA-DDM-aGO})}/k_{2(\text{DGEBA-DDM-aGO})}}{bk_{1(\text{DGEBA-DDM})}/k_{2(\text{DGEBA-DDM})}} = \frac{2.13}{1.33} = 1.60 = \frac{bk_{1(\text{DGEBA-DDM-aGO})}}{bk_{1(\text{DGEBA-DDM})}} \times \frac{k_{2(\text{DGEBA-DDM})}}{k_{2(\text{DGEBA-DDM-aGO})}}$$

Since the ratio of the 1° amine consumption rate for DGEBA-DDM-aGO to that for DGEBA-DDM is given in **Table 4.3** as 0.88 then:

$$\frac{k_{2(\text{DGEBA-DDM})}}{k_{2(\text{DGEBA-DDM-aGO})}} = \frac{1.60}{0.88} = 1.82 = 1/k_{2(\text{rel})}$$

Therefore the rate coefficient of 2° amine reaction in aGO nanocomposite compared to neat resin is 0.55. The other values of $k_{2(\text{rel})}$ in **Table 4.4** may be determined in the same way.

It was hypothesised that the slower consumption of 2° amine in aGO could be attributed to two factors ie; covering of reactive sites by OD and steric hindrance arising from the GO sheets themselves. The steric hindrance can occur when aGO, after reaction with one 1° amine group will be sterically hindered for reaction of the formed 2° amine with another epoxy group owing to the bulky structure of GO. However, considering the close similarity of the $k_{2(\text{rel})}$ values for the DGEBA-DDM-OD system and the DGEBA-DDM-aGO nanocomposite (**Table 4.3**) the difference in the rate of 2° amine reaction is mainly accounted for by physical covering of epoxy groups in aGO by adhered OD in a similar way as for the 1° amine-epoxide reaction.

In addition if steric hindrance was a factor, slower consumption of 2° amine would be expected in DGEBA-DDM-acGO nanocomposite as well but we actually observed faster consumption in that system. So, it tells us that the steric hindrance effect is not dominant and greater effect would have arisen from the hiding of active sites by OD.

Of importance in this discussion is the point at which the resin gels since the 2° amine-epoxide reaction may then become diffusion controlled. The theoretical conversion (α_{gel}) for gelation of a stoichiometric di-epoxide/di-amine system is between 0.5 and 0.6 depending on the ratio k_1/k_2 .⁴⁹ From **Figure 4.8(a)** this corresponds to between 10 and 13 min for the neat amine-cured resin. The considerable slowing in 2° amine reactivity seen in **Figure 4.11** from all systems is therefore also occurring around the time for the onset of gelation. Separating the physical from chemical effects on the reaction rate is therefore difficult.

4.5.3.4 3° amine formation

The comparative reactivity of the 2° amine groups (**Figure 4.1**, reaction 2) in the bulk resin and the interphase may be assessed by computing the concentration-time profiles of 3° amine arising from the difference between the concentrations of 1° amine and 2° amine at each time during cure using equation 16.

$$a[3^\circ A]_t = [1^\circ A]_0 - [1^\circ A]_t - b[2^\circ A]_t \quad (16)$$

It is noted that the results presented in **Figures 4.8** and **4.10**, the emitted IR radiation will be occurring from both the resin that is within the interphase region as well as from any “bulk” resin away from the interphase. We have calculated the interphase fraction of aGO-epoxy nanocomposite based on the aGO addition of 0.3 wt% and an interphase thickness of 118 nm.¹¹ The interphase fraction is calculated as 30% (based on a cured resin density of 1.16 g/cm³ and the measured surface area of 719 m²/g, given in supporting information).

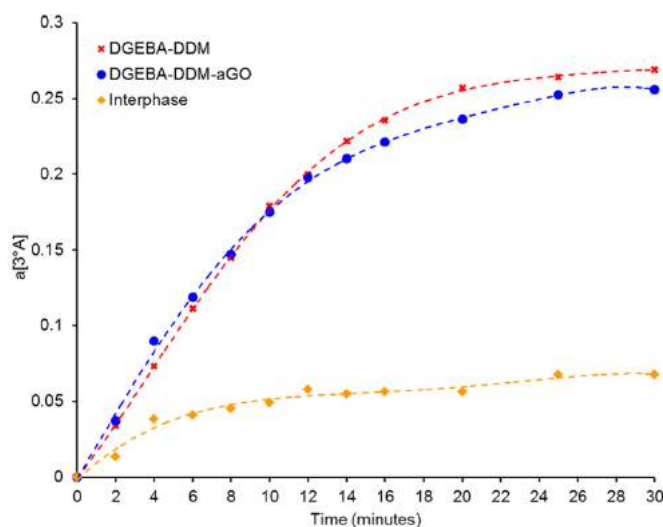


Figure 4.12. Calculated 3° amine concentration during the cure at 100°C for 30 minutes of DGEBA-DDM (-x-), DGEBA-DDM-aGO (-•-) and the interphase DGEBA-DDM-aGO based on 30% interphase contribution from surface area measurements (-o-). Dashed lines represent the trendline of the individual curves.

Figure 4.12 shows the 3° amine profiles for the two systems DGEBA–DDM and DGEBA-DDM-aGO computed from the FT-IES emission intensities in **Figures 4.10(a)** and **4.11**. As discussed above, the profile measured for the DGEBA-DDM-aGO system comprises 70% from the bulk and 30% from the interphase. By allowing for this “bulk” contribution the 3° amine profile from the interphase region may be computed and is also shown in **Figure 4.12**. This profile is particularly interesting as it shows that the 2° amine reaction to produce 3° amine in the aGO-epoxy resin interphase is significantly retarded compared to the bulk resin with the reaction significantly slowing after the first 10 minutes of cure. This will result in a much lower crosslink density of the network in the interphase region since it is the 2° amine reaction to produce 3° amine that results in the final reactivity and complete cure of the network. This will have consequences for the structure of the interphase since lower crosslink density will affect both T_g and the micromechanics, particularly toughness. Since diffusion control is occurring in both the neat resin and the interphase reactions, this effect is in addition to any physical effects on the cure rate.

4.5.4 DSC study of extent of cure and T_g

The dynamic DSC heat flow curves of the DGEBA –DDM, DGEBA -DDM-aGO and DGEBA -DDM-acGO systems which are partially cured at different time

intervals were obtained. **Figure 4.13(a)** represents the DSC heat flow curves of DGEBA-DDM-aGO (The heat flow curves of other two systems are given in **Figure 4.20**, supporting information). We have noticed that onset of the cure reaction (T_{onset}) increased in aGO-epoxy system ($\sim 108^{\circ}\text{C}$) whereas it decreased in acGO-epoxy system ($\sim 102^{\circ}\text{C}$) compared to neat epoxy (103°C). This indicates the acceleration effect in acGO and retardant effect by aGO on cure reaction as described at length in Section 4.5.3. However, ΔH_{cure} and the peak heat flow (T_p), ie., the temperature of maximum heat flow during the cure reaction, remained largely unaffected. Significantly, we observed the heat capacity change corresponding to the appearance of T_g of the epoxy resin with the partial curing for 10-15 min or longer at 100°C (arrowed in **Figure 4.13(a)**). The effect of aGO and acGO on the network structure and T_g is discussed further below.

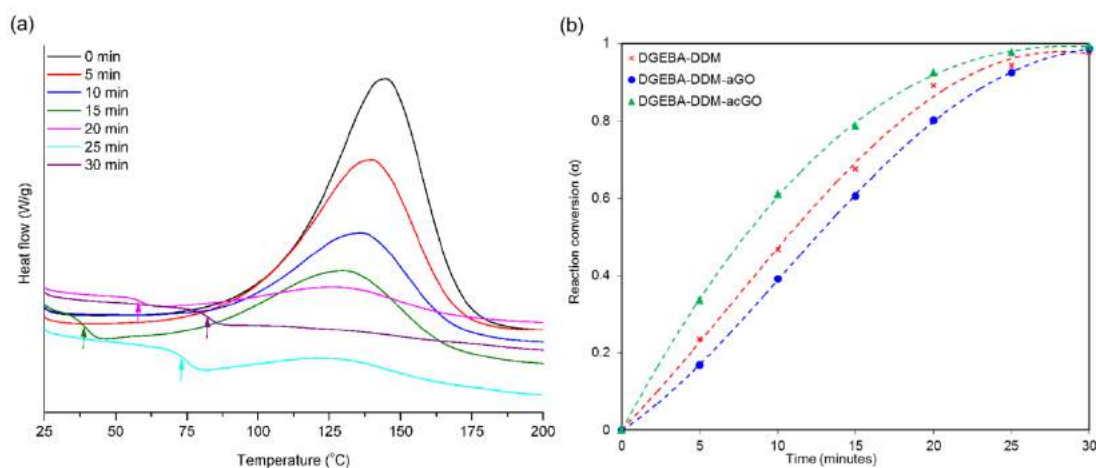


Figure 4.13. (a) DSC thermograms of DGEBA-DDM-aGO at different partially cured time intervals showing the appearance of the glass transition temperature, T_g (small arrows) as well as the decrease in the heat evolution with increased time of cure (starting from top curves) (b) Comparison of reaction conversion by DSC of DGEBA-DDM (-x-), DGEBA-DDM-aGO (-•-) and DGEBA-DDM-acGO (-▲-) at different curing times, showing a lower extent of cure in the presence of aGO and a higher extent of cure in the presence acGO for the same time of cure. Dash lines represent the trendline of the individual curves.

We have calculated the extent of conversion of the cure reaction (α) as a function of initial curing time using these heat flow curves and **Figure 4.13(b)** shows the calculated data for DGEBA-DDM, DGEBA-DDM-aGO and DGEBA-DDM-acGO nanocomposites. It can be observed that values of α for DGEBA-DDM-aGO at all curing time intervals are lower than those of DGEBA-DDM. This suggests that

curing reaction of epoxy was slowed down with incorporation of aGO into the epoxy matrix, consistent with the FT-IES results of Section 4.5.3. In contrast, addition of acGO into the epoxy matrix sped up the cure reaction producing higher values for α at the same cure time. These results further confirmed the FT-IES result that acGO can accelerate the curing reactions. Therefore, it can be seen that the presence (or absence) of OD on the GO surface greatly influences associated kinetic processes. A recent study reported the influence of OD on the kinetic process of nucleation and growth of Ag nanoparticles (AgNPs) on graphene oxide. They found that the formation of larger AgNPs on OD-free GO surface compared to smaller AgNPs on as-prepared GO. This indicates that OD plays a key role in the energetic stabilization process that allows the formation of small nanoparticles.⁵⁰

T_g and reaction conversion of epoxy and its nanocomposites at different curing time interval are shown in **Table 4.5**. In addition, T_g of completely cured neat epoxy, aGO-epoxy and acGO epoxy nanocomposites were measured as $\sim 92^\circ\text{C}$, $\sim 83^\circ\text{C}$ and 105°C , respectively. It is clear that T_g of the aGO nanocomposite is significantly lower than that of neat epoxy matrix whereas the acGO nanocomposite has significantly higher T_g . Lower T_g is attributable to the lower cross-link density of the epoxy matrix structure in as-prepared GO nanocomposites. As discussed earlier, aGO can slow down the formation of the 3D network structure in epoxy matrix, especially near the interphase region between epoxy and aGO. This results in the presence of more linear polymer chains (**Figure 4.1**, reaction 1) which have a higher polymer chain mobility compared to cross-linked structures (**Figure 4.1**, reaction 2) from reaction of the 2° amine. The higher chain mobility in the polymer matrix results in a decreased T_g of the epoxy matrix. It should be noted that as discussed above in the FT-IES study, the fraction of the resin that is in the interphase region is only 30% of the total volume of resin so the effect on the lower crosslink density of the resin in this region on the overall T_g is significant. This again shows the less brittle structure of epoxy matrix in aGO nanocomposite. Furthermore, presence of OD in aGO can speed up the homopolymerization which also contribute to the formation of more linear polymer chains. On the other hand, acGO accelerates the cure, particularly the 2° amine reaction, resulting in a higher crosslink density network and consequently, more brittle structure and higher T_g .

Table 4.5. Change of T_g and reaction conversion rate at different curing time interval of DGEBA –DDM, DGEBA -DDM-aGO and DGEBA -DDM-acGO.

Time (t, min)	DGEBA-DDM		DGEBA-DDM-aGO		DGEBA-DDM-acGO	
	α	$T_g(^{\circ}\text{C})$	α	$T_g(^{\circ}\text{C})$	α	$T_g(^{\circ}\text{C})$
0	0	-	0	-	0	-
5	0.23	-	0.17	-	0.34	-
10	0.47	-	0.39	-	0.61	42
15	0.68	53	0.60	40	0.79	59.5
20	0.89	74	0.80	60	0.92	72.5
25	0.94	83	0.92	76	0.98	88.5
30	0.98	93	0.99	83	0.99	92

Therefore, we believe that in the presence of aGO, formation of three dimensional network structures in the epoxy matrix slows down, particularly near the aGO-epoxy interphase region. So the region immediately around the aGO (interphase) will have a lower crosslink density and thus a higher toughness. As a result, aGO nanocomposite shows significantly higher toughness than neat epoxy. Increase of toughness with addition of aGO into epoxy matrix has been reported in literature.^{15, 18, 51-52} Moreover, low crosslink density of epoxy matrix can lower the T_g of the polymer matrix. Removal of OD from aGO by autoclaving (to give acGO) reversed the overall effect of aGO by accelerating cure process, giving a more cross-linked matrix structure, lower toughness and higher T_g . The OD clearly has a major role to play in the performance of nanocomposites by acting as a compatibilizing surfactant which is beneficial in producing nanocomposites with a good dispersion and a toughened interface between GO and a polymer matrix.⁵³

4.6 Conclusions

We have reported a simple and quick FT-IES method to monitor the cure kinetics of epoxy curing and to evaluate the influence of aGO and removal of OD on the network formation and the rate of reaction. The technique offers an immediate assessment of the chemical changes occurring in the matrix while curing progresses. Emission spectra clearly showed the gradual decrease of peak intensities of epoxide, 1° and 2° amine bands with the time of curing as well as the increase and broadening

of ether bands. This indicates the consumption of epoxide and amine groups to form the cross-linked resin matrix. Further, the comparison studies revealed the retardant effect of aGO on the epoxy curing, principally on the reaction of the formed 2°amine with further epoxide. The retardant effect of aGO on 2° amine reactions has been linked to this oxidative debris which also enhances etherification reactions such as homopolymerization which also lowers the crosslink density in the interphase. Removal of OD from aGO sped up overall cure process, consequently crosslink density in the epoxy matrix. There was evidence that OD significantly covered the available reactive and catalytic sites in aGO surfaces and greatly influenced the catalytic behaviour of GO.

FT-IES data have been confirmed by DSC studies where aGO-epoxy nanocomposite exhibited considerably lower T_g and the slower conversion of reaction compared to neat epoxy. Removal of OD caused an increase of the cross-link density in the epoxy matrix, consequently higher T_g and brittle material.

Therefore, it can be concluded that these chemical changes in the interphase compared to bulk are consistent with the result that low addition of aGO (commonly used as GO in polymer nanocomposites) can effectively improve the toughness of epoxy matrix. This work highlights the importance of oxidized debris in affecting the chemistry of the cure reactions leading to novel interphase structure.

4.7 Acknowledgement

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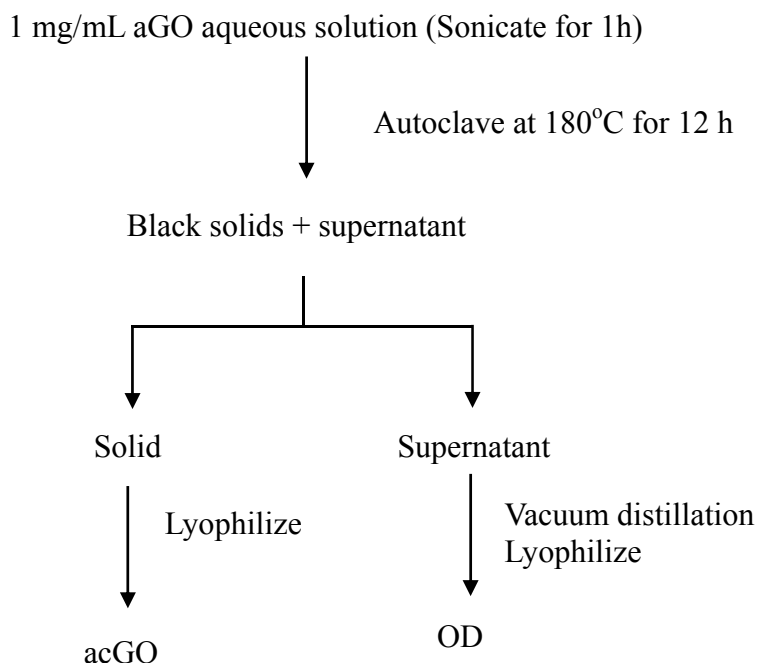
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4.9 Supporting information

Preparation of GO

GO was prepared by oxidation of graphite flakes according to the modified Hummers method.¹ In brief, a mixture of graphite and KMnO_4 (Ratio of 1:6) was added into a beaker containing mixture of H_2SO_4 : H_3PO_4 (9:1) acids. Then the reaction mixture was stirred while heating at 50°C for 12 h. The reaction mixture was cooled down to room temperature and poured onto ice cubes with 3 ml of 30% H_2O_2 . Then the mixture was sieved through a metal US standard testing sieve ($250\ \mu\text{m}$). The filtrate was centrifuged at 4000 rpm for 30 minutes. The precipitate was washed with DI water, HCl and ethanol. For each wash, the mixture was sieved through US standard testing sieve followed by centrifuging at 4000 rpm for 30 min. The final precipitate was dissolved in DI water and sonicated for 1 h. Finally, the GO aqueous dispersion was freeze for 24h followed by freeze drying at -51°C under vacuum condition for 72 h. The final product is called as aGO.

Preparation of acGO and isolation of OD



acGO was prepared as shown in the above flow chart and isolated debris named as Oxidative debris (OD). We produced base washed GO (bwGO) following the procedure reported elsewhere²⁻⁵ to compare with acGO.

Characterization of aGO and acGO

X-ray photoelectron spectroscopy measurements were performed with a Kratos Axis ULTRA X-ray photoelectron spectrometer (XPS) using monochromatic Al- $\kappa\alpha$ radiation ($h\nu = 1486.6$ eV). CasaXPS v 2.3.16 software was used to perform curve fitting and to calculate the atomic concentrations. X-ray diffraction (XRD) powder patterns were taken on a conventional X-ray diffractometer (XRD, PANalytical Cu MPD) using Cu $\kappa\alpha$ radiation. Raman spectra of samples were recorded from 1250 to 3000 cm^{-1} on a Renishaw inVia Raman Microscope using a 532 nm edge filter laser beam. IR spectra were obtained using FTIR 5700 Nicolet Diamond ATR spectrometer. The spectrum resolution was 4 cm^{-1} in the range from 800 to 4000 cm^{-1} . 64 scans were performed to get the average spectrum. The microstructural characterizations were performed using a JEOL-7001F field-emission scanning electron microscope (FESEM) operated at 15 kV and a JEOL 1400 transmission emission microscope (TEM) operated at 120 kV. Dry aGO powder was used for the FESEM analysis. Clear solution of aGO in DMF was dropped cast onto carbon coated copper TEM grid for TEM analysis. Samples for atomic force microscope (AFM) imaging were prepared by depositing clear solution of aGO (in DMF) on freshly cleaved mica surface. AFM images were taken using a BMT multi-scan AFM with silicon tip. Tapping mode was applied to get the topography of the GO flakes at the scan rate of 1.2 Hz with surface area of $5 \times 5 \mu\text{m}^2$.

Surface area of aGO was measured, by the MB method reported by Navajas et al.⁶ starting from an aqueous dispersion of a known weight of aGO to which increasing amounts of MB were added, following the evolution of the visible transmittance spectra. Concentrations of aGO dispersions were 0.043 and 0.085 $\mu\text{g}/\mu\text{l}$ and concentration of stock aqueous solution of MB was 0.3 $\mu\text{g}/\mu\text{l}$. Transmittance spectra were recorded by placing 2 ml of aGO aqueous solution in 1cm path length quartz cuvette and adding small aliquots (5 μl initially and 1 μl near end point) of MB stock aqueous solution of 0.3 $\mu\text{g}/\mu\text{l}$ under continuous magnetic stirring, using an Ocean USB4000 Fibre Optics spectrometer. The baselines of the spectra were corrected by subtracting the initial aGO transmittance and then transmittance spectra were converted to absorbance. The addition of MB was continued up to blue precipitation. The value of the amount of MB corresponding to

the maximum intensity of the 580 nm band was taken as indicative of complete surface coverage of aGO.⁶

Results

XPS analysis

XPS analysis was employed to detect oxygen contents and micro-chemical environment of aGO and acGO. The atomic composition of aGO and acGO was obtained from survey spectra and O/C ratio was observed as ~ 0.45 for aGO and ~ 0.17 for acGO in good agreement with earlier work.^{2, 7-10} The spectrum of aGO was deconvoluted by using five peaks assigned to non-oxygenated C (C-C, 284.3 eV), C attached to COO (C*-COO, 285.3 eV) epoxy and hydroxyl groups (C-O, ~ 286.7 eV), carbonyl groups (C=O, ~ 287.9 eV) and carboxylate groups (COO, 288.5 eV). Similarly, XPS spectrum of acGO shows one main peak at 284.5 eV (C-C), and three small peaks at 286.2 eV, 287.9 eV and 288.9 eV. These peaks can be assigned to C-O, C=O and π - π shake-up bands, respectively.⁸ However, these peaks are considerably smaller compared to those of aGO which indicate that the quantity of oxygen moieties in aGO decreases after the removal of OD. In comparison, a similar reduction of degree of oxidative functionality was reported for bwGO.^{2, 11-12} Rourke et al., found that C: O ratio reduced from 2:1 in aGO to 4:1 in bwGO.² Similarly, Faria et al. reported that the integrated intensity ratio between C-C and C-O is 1.45 for aGO and 1.73 for bwGO.⁴ Our XPS data on acGO is comparatively closed to those reported for bwGO.

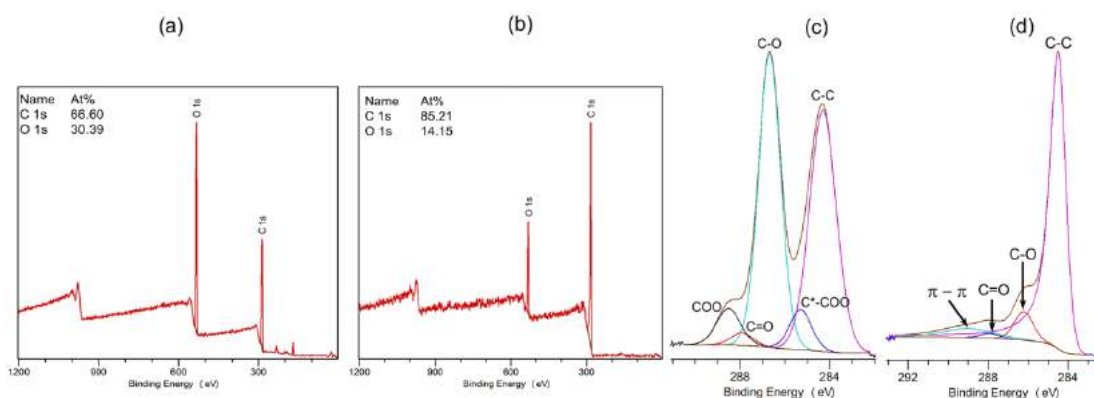


Figure 4.14. XPS survey of (a) aGO (b) acGO, C 1s XPS spectra of (c) aGO and (d) acGO.

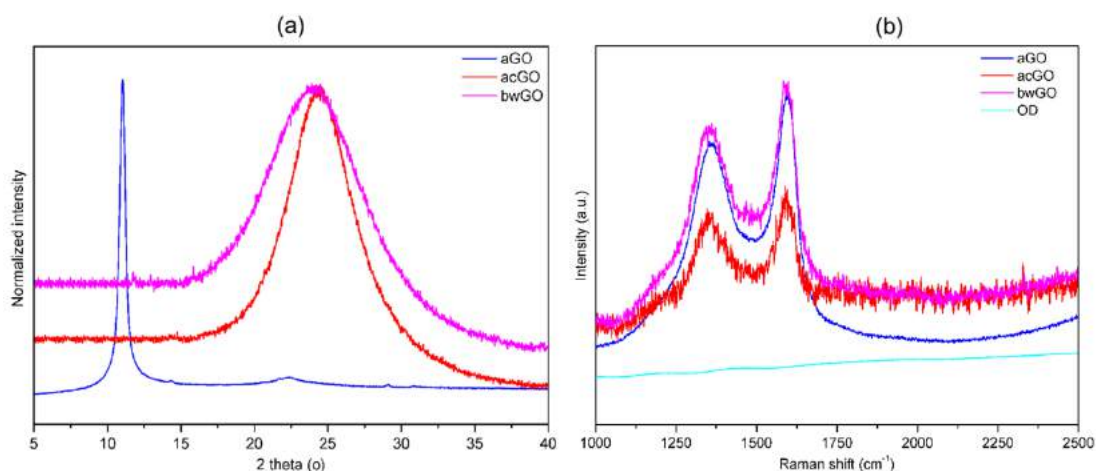


Figure 4.15. (a) XRD of aGO, acGO and bwGO (b) Raman of aGO, acGO, bwGO and OD.

To analyse the effect of purification processes on the interlayer structure, we obtained the XRD pattern of the samples, **Figure 4.15(a)**. aGO diffractogram presents a peak around 11° . This peak is characteristic of 002 plane of graphite compounds and the interlayer distance calculated is ~ 0.93 nm. This value is similar to graphene oxide reported in literature.¹³⁻¹⁴ The purification process leads to a shift towards higher angle value of the (002) diffraction peak. The interlayer distance values for acGO and bwGO were 0.36 and 0.37 nm, respectively indicating that the purification process decreases the interlayer distance. This could be due to the elimination of the OD located at the interlayer.¹² It also confirmed that both purification processes resulted in similar product.

The spectra in **Figure 4.15(b)** show the two characteristic raman bands of graphene derivatives, centred at 1597 cm^{-1} (G band) and 1350 cm^{-1} (D band) respectively. The value of I_D/I_G ratio was almost identical for all three samples, ie. aGO, acGO and bwGO (~ 0.77) suggesting that the graphene sheets are not altered themselves by purification.^{2, 12} The raman spectra of OD does not show any evidence of G or D bands.³

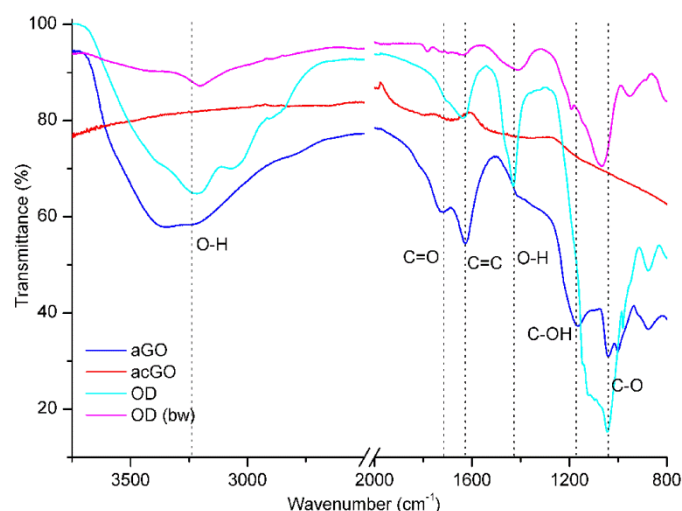


Figure 4.16. FTIR of aGO, acGO and OD.

As shown in **Figure 4.16**, the FTIR transmittance spectrum of aGO shows a broad peak at $3800\text{--}2500\text{ cm}^{-1}$ (OH and H_2O) and several peaks between 1800 and 800 cm^{-1} . These peaks can be assigned to carboxyl, ketone, hydroxyl, epoxide and C=C bonding as labelled in the figure.^{2-3, 11-12} The FTIR spectra of both ODs (from autoclaved and base washed) are similar to that of aGO, even as the spectrum of acGO is comparatively featureless. Therefore, we conclude that OD contains heavily oxidized with similar functionalized groups to aGO and degree of functionalization is decreased with purification processes.

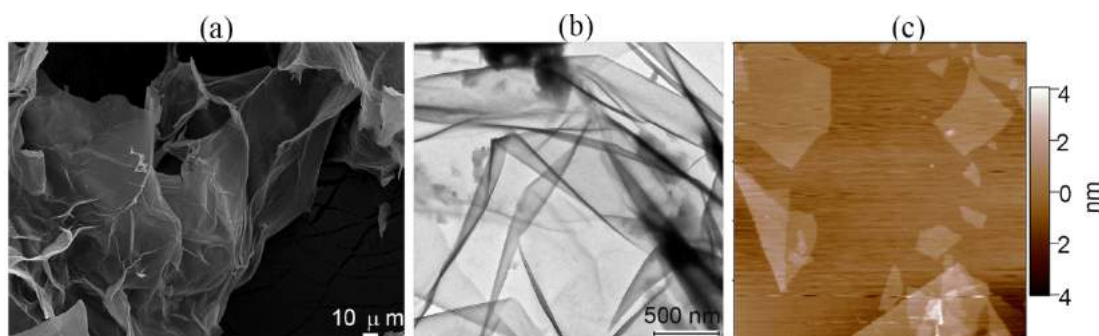


Figure 4.17. (a) SEM (b) TEM (c) AFM images of aGO.

Figure 4.17 illustrates typical SEM, TEM and AFM micrographs of aGO.^{1, 15} Generally, morphology of graphene sheets is not affected by purification process. But there should be some changes in layer thickness of the sheets in purified GO which would be able to observe by AFM topography.⁴

Surface area measurements of aGO

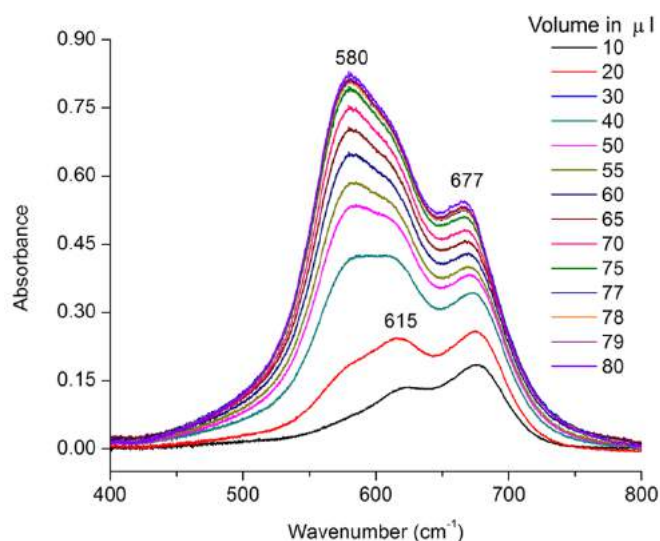


Figure 4.18. Visible absorption spectra of aqueous dispersion of aGO (a) 0.043 $\mu\text{g}/\mu\text{l}$ upon addition of increasing volume of a MB stock solution (0.3 $\mu\text{g}/\mu\text{l}$). The baseline of the spectra has been corrected subtracting the initial aGO absorption.

Surface area of GO was calculated using the changes in UV Visible absorption spectra of an aqueous aGO solution upon the addition of MB. We observed identical spectra and spectral changes with MB addition as reported by Navajas et al.⁶ At low MB concentration, two peaks were observed at 667 nm and 615 nm which are attributed to aGO and MB π clouds overlapping and interactions between MB molecules adsorbed on aGO. With increasing MB concentration a new peak appeared at 580 nm, which is attributed to close packing of MB on upper and lower surfaces of aGO. Further addition of MB, increased the intensity of latter peak and the maximum intensity was observed just before the formation of a blue colour precipitate suggesting complete surface coverage of aGO by MB adsorption (**Figure 4.18**). The amount of MB used up at maximum intensity is 79 μl and estimated surface area of aGO is 719 m^2/g considering 2.54 m^2 as the area covered by 1 mg of MB.^{6, 16} Calculated surface area of aGO is comparable to values reported in literature.^{6, 16}

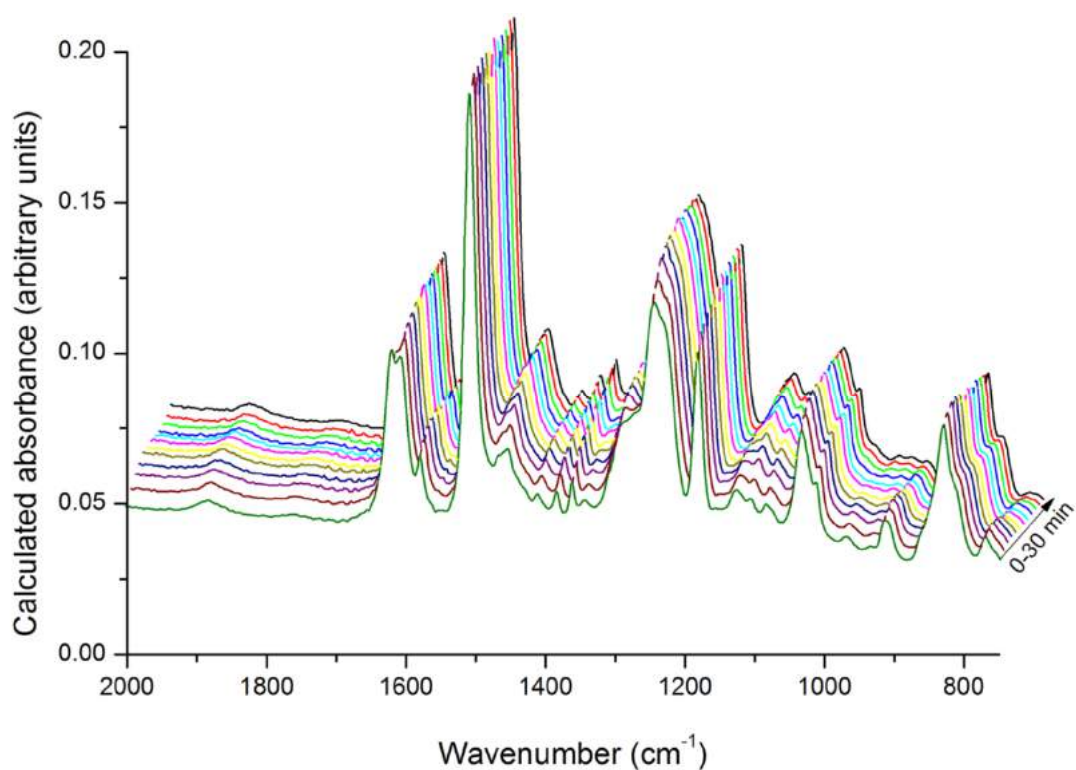


Figure 4.19. Stack plot of successive spectra of DGEBA-DDM-aGO at 100 °C for cure up to 30 minutes.

Figure 4.19 illustrates the spectra of DGEBA-DDM-aGO at 100 °C for cure up to 30 minutes. Similar spectra were observed for DGEBA-DDM-acGO and DGEBA-DDM-OD.

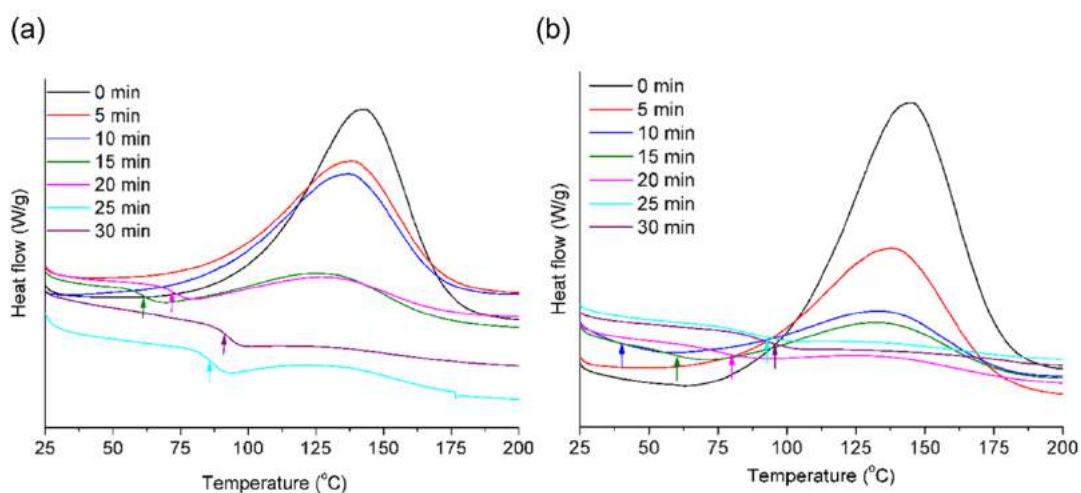


Figure 4.20. DSC thermograms of (a) DGEBA-DDM (b) DGEBA-DDM-acGO at different partially cured time intervals showing the appearance of the glass transition temperature, T_g (small arrows) as well as the decrease in the heat evolution with increased time of cure (starting from top curves).

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5 Graphene-Based Thin Film Supercapacitor with Graphene Oxide as Dielectric Spacer

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5.1 Prelude

A capacitor is a passive two-terminal electrical component used to store energy electrostatically in an electric field. Generally, capacitors contain at least two electrical conductors separated by a dielectric (i.e. insulator). Solid state film capacitors use solid dielectric spacer such as plastic films. The thickness of the plastic film typically ranges from 2 μm to 20 μm . However, due to the low dielectric constant and larger thickness of plastic spacer, such film capacitors usually have low capacitance.

GO is an insulating material with high dielectric constant. It is also possible to make GO films with thickness less than 1 μm which is much thinner than plastic layer.

In this paper, we investigated use of GO as a dielectric spacer in film supercapacitors utilizing its high dielectric constant and electric resistivity.

5.2 Statement of Contribution

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of the journals or other publications and (c) the head of the responsible academic unit, and

5. they agree to the use of publication in the student's thesis and its publication on the Australia Thesis Database consistent with any limitation set by publisher requirements.

In the case of this chapter:

Graphene-based thin film supercapacitor with graphene oxide as dielectric spacer

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Contributor	Statement of contribution
Jinzhang Liu	Fabrication and characterization of supercapacitor, data analysis, paper writing
Dilini Galpaya	Nanoparticle synthesis and characterization
Marco Notarianni	data analysis, paper writing
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Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Cheng Yan



16/6/15

Name

Signature

Date

Abstract

Thin film supercapacitors are produced by using electrochemically exfoliated graphene (G) and wet-chemically produced graphene oxide (GO). Either G/GO/G stacked film or sole GO film are sandwiched by two Au films to make devices, where GO is the dielectric spacer. The addition of graphene film for charge storage can increase the capacitance about two times, compared to the simple Au electrode. It is found that the GO film has very high dielectric constant, accounting for the high capacitance of these devices. AC measurements reveal that the relative permittivity of GO is in the order of 10^4 within the frequency range of 0.1–70 Hz.

5.3 Introduction

Graphene, a two dimensional carbon material, with excellent mechanical, thermal, and electrical properties,¹⁻³ is an ideal candidate for developing novel devices. Large-scale production of graphene is normally via the wet-chemical production of graphene oxide (GO) using graphite powder as precursor, and then the reduction of GO to improve the conductivity. GO sheets behave like insulators, with differential conductivity values of $1-5 \times 10^{-3}$ S/cm depending on the oxidation degree.⁴ Reduced GO (rGO) has been used as an electrode material to make supercapacitors for energy storage. rGO electrodes can be obtained in several ways: a) by electrolyzing GO aqueous suspension containing LiClO_4 to coat porous rGO film onto a gold foil;⁵ b) by vacuum filtration of rGO suspension to produce a film;⁶ c) by thermal reduction of GO films by laser scribing.⁷ In most cases graphene electrodes are used in electrochemical supercapacitors. In device fabrication, an electrolyte layer is sandwiched by two rGO electrodes. In comparison, solid state capacitors that use solid dielectric spacer are very simple to fabricate. Film capacitors are conventionally made out of plastic films covered with metallic layers. The thickness of the plastic film typically ranges from 2 μm to 20 μm . Due to the low dielectric constant of the plastic spacer and large thickness, such film capacitors usually have low capacitance. Though the electrical conduction and high surface-to-volume ratio of graphene play an important role in developing supercapacitors, it is worth exploiting also the insulating properties of GO with the aim of making all-graphene capacitors. It was reported that the polymer poly(vinylidene fluoride) containing graphite oxide

nanoplates, produced by chemical oxidation of graphite with concentrated sulfuric acid and nitrate acid and following exfoliation, show high dielectric permittivity with an order of 10^4 if the volume fraction of nanoplates is 1.5%.⁸ It implies that the dielectric constant of GO may be very high. Sole GO film can be prepared with thickness less than 1 μm -thick, much thinner than the plastic layer in thin film capacitors. We believe that the use of GO film as thin spacer in a double-layer capacitor can improve the capacitance.

A greener method for producing graphene is the electrochemical exfoliation of graphite, which is optional in terms of electrolyte and experimental conditions. The electrochemical exfoliation using aqueous electrolyte is fast and simple, and can produce graphene sheets with high quality comparable to rGO.⁹ Herein, we report thin film capacitors made by combining electrochemically exfoliated graphene with wet-chemically produced GO and by using GO film as dielectric spacer. The effect of graphene electrode on enhancing the capacitance and the dielectric constant of GO are investigated.

5.4 Experimental

The GO was produced by a modified Hummer's method as described in literature.¹⁰ The final GO product was dispersed in dimethylformamide (DMF) to form a stable suspension. To produce graphene using the electrochemical exfoliation method, a piece of highly ordered pyrolytic graphite ($1 \times 1 \text{ cm}^2$) and a Pt wire are used as electrodes. The electrolyte is a 150 ml aqueous solution containing 0.15 M Na_2SO_4 and 0.01 M sodium dodecyl sulfate. The pH value of the electrolyte was adjusted to ~ 2.0 by adding few drops of sulfuric acid. With 5-6 V bias, the HOPG expanded quickly and was thoroughly consumed within one hour. After the exfoliation, the dark-colour electrolyte was centrifuged at 3000 rpm for 30 min to remove large agglomerates. The remaining dispersion was further diluted with DI water and vacuum filtered onto a porous polymer membrane. The black product obtained in this way was ultrasonically dispersed in DI water and filtered again. This process was repeated three times to ensure the removal of chemical residues. Afterwards, the product was dispersed in DMF.

Suspensions of GO or electrochemically exfoliated graphene (G) are used to make either GO or G/GO/G stacked films by using a vacuum filtration method.

The film thickness onto the porous alumina membrane (Whatmann Co., pore size 100 nm) can be controlled by the volume of suspension for filtration. **Figure 5.1 (a)** illustrates the device fabrication. First, an electrode (80 nm-thick) is obtained by sputtering Au onto a glass substrate through a shadow mask. Second, the GO or G/GO/G stacked film is transferred from the porous membrane onto the Au-covered glass substrate. The transfer involves etching away the alumina membrane in a NaOH aqueous solution, leaving the graphene film floating in the solution surface. After washing away chemical ions the film is transferred onto the Au-coated glass substrate. Finally, a gold film (80 nm-thick) is deposited onto the dried GO or G/GO/G stacked film. The capacitor area is 0.12 cm². Two types of devices, D1 and D2, with different structures were made as shown in **Figure 5.1 (b)** and **1(c)**, respectively. D1 is made out of G/GO/G stacked films, in which each graphene layer is 25-nm-thick and the GO spacer is 350-nm-thick. D2 is made out of a 400-nm-thick GO film.

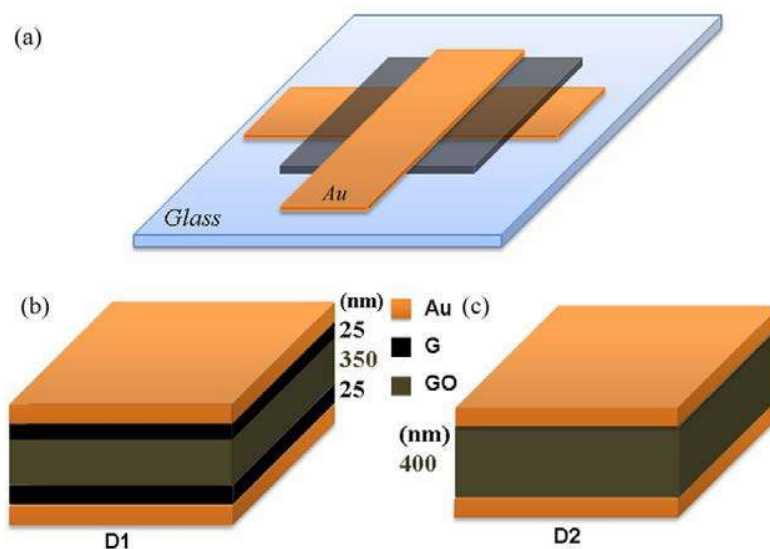


Figure 5.1. (a) Illustration for the device fabrication. (b, c) Structures of two devices with different spacer thickness.

5.5 Results and discussion

We tested a 100 nm GO film and a 100 nm electrochemically exfoliated graphene film on glass substrates by four-probe sheet resistance measurement. The sheet resistance of the GO film is in the order of MΩ/sq, and that of the graphene film is KΩ/sq. We conclude that the graphene we made is comparable to rGO in electrical conduction.¹¹ Field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma VP) images of the GO and G/GO/G stacked films are shown in

Figure 5.2. A top-view FE-SEM image of a GO film is shown in **Figure 5.2 (a)**. We tore the films to observe their cross-sections and to measure their thickness by FE- SEM. **Figure 5.2 (b)** shows a tilt-view of a free-standing G/GO/G stacked film.

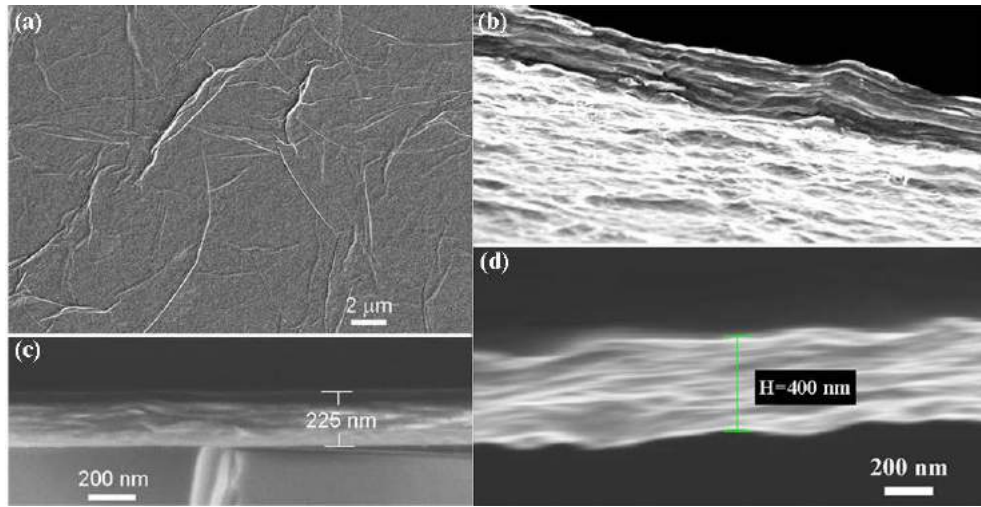


Figure 5.2. FE-SEM images of graphene films. (a) Top view image of a GO film. (b) Tilt-view image of a free-standing G/GO/G stacked film. (c) Side-view image of a GO film on Si substrate for more accurate measurement of the thickness. (d) Cross-section of the free-standing film as in (b).

The capacitor performance of the two devices, D1, and D2, were analyzed using cyclic voltammetry (CV), from which the capacitance can be extracted. **Figures 5.3 (a) and 5.3 (b)** show the CV curves of D1 and D2, respectively. CV scans were conducted from -1 V to +1 V with scan rates of 20, 50, 200, and 500mV/s. These loop curves demonstrate quasi-rectangular shapes, indicating double-layer capacitive behaviours. **Figure 5.3 (c)** shows the Nyquist impedance spectrum of the two devices, measured with AC frequency range from 0.05 Hz to 1M Hz. The inset is expanded view of the region at high frequency, showing that both devices have low equivalent series resistance of $\sim 16 \Omega$. Relationships of impedance phase angle versus frequency for the three devices are compared in **Figure 5.3 (d)**. If we treat the capacitor as a parallel RC circuit, the phase angle can be expressed as $\theta = \tan^{-1}(I_c/I_R)$, where I_c and I_R are the current values through the capacitor and the resistor, respectively. The phase angle different from $\pi/2$ indicates that a current flows through the GO film. We believe that the resistance of the GO spacer can be further increased by enhancing the oxidation degree of GO or by integrating GO with other insulating materials. It is noticeable that D2 maintains phase angle below -60° even $f > 1$ kHz. Whereas for an activated

carbon double-layer capacitor, the phase angle decreases rapidly with frequency in a small range of 0-10 Hz.¹²

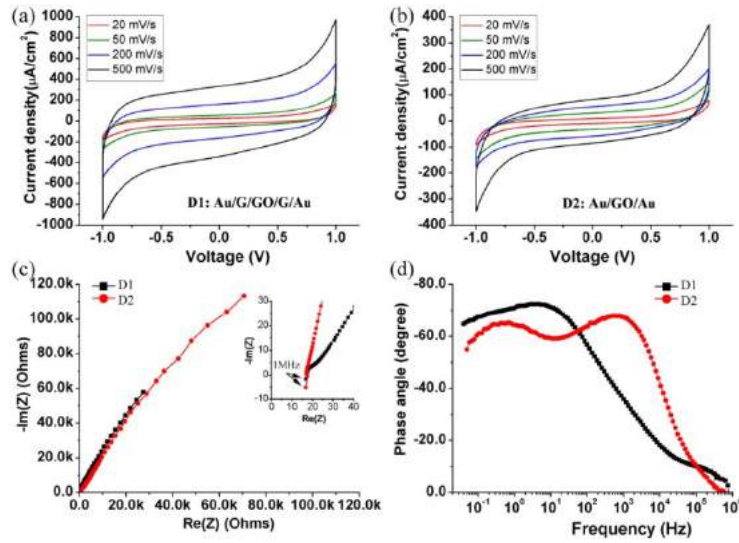


Figure 5.3. (a and b) Cyclic voltammetry curves for two devices, D1 and D2, respectively. (c) Impedance spectrum of the two devices. (d) Phase angle change versus frequency for the two devices.

The capacitance can be calculated from the CV curve by using the current I and scan rate dV/dt , as $C=I/(dV/dt)$, where the value of I is taken at $V=0$. The specific capacitance against scan rate for the two devices is plotted in **Figure 5.4 (a)**. Overall, the capacitance decreases with the scan rate from 10 mV/s to 500 mV/s. D1 and D2 have the same interdistance (400 nm) between the two opposite Au films. However, the capacitance of D1 is over two times that of D2 because of the added graphene film between GO and Au. Cheng *et al* studied the electrochemical interfacial capacitance in multilayer graphene sheets and pointed out that the use of thick graphene sheets can enhance the capacitance.¹³ Yoo *et al* made ultrathin planar graphene supercapacitors and the measured capacitance for 1-2 layer graphene and multilayer rGO electrodes are up to $80 \mu\text{F}/\text{cm}^2$ and $394 \mu\text{F}/\text{cm}^2$, respectively.¹⁴ For bulk graphite the higher interfacial capacitance on edge plane than basal plane was observed.¹⁵ In our work, the electrochemically produced graphene consists of few-layer and multilayer flakes. The screening length for pristine graphene was measured about 1.2 nm.¹⁶ For the graphene flakes that we produced, their conductivity is less than pristine graphene and thus the screening length would be larger. Inside the graphene film (~ 25 – 21 nm-thick) made by vacuum

filtration, graphene flakes are compactly stacked and charges are stored not only at the G/GO interface but also at inner flakes and mainly at the edges, with the presence of an electric field. Hence, a space charge region in the graphene film contributes to higher capacitance, compared to the use of sole Au electrode.

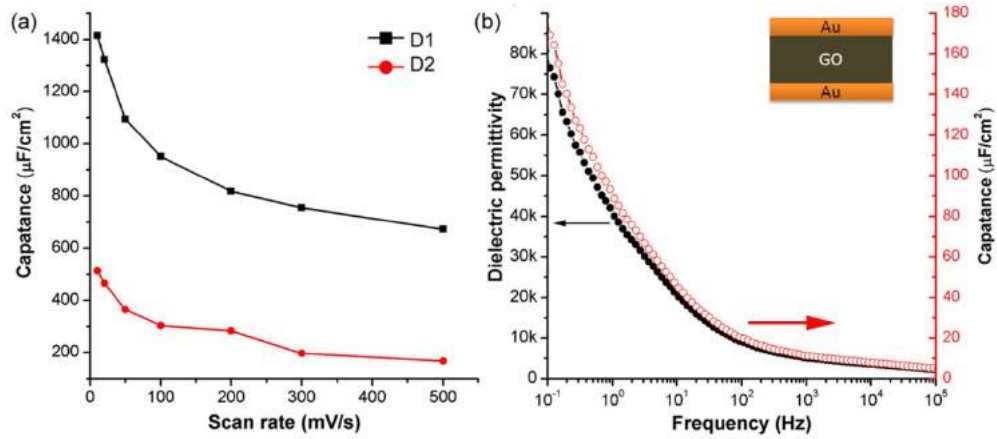


Figure 5.4. (a) Capacitance of the two devices against different voltage scan rates, calculated from the cyclic voltammetry curves. (b) Capacitance versus AC frequency curve of D2, obtained from the imaginary part of impedance. The relative permittivity of GO film is deduced and plotted by the open- circle curve.

Without using graphene film, D2 with the Au/GO/Au structure shows specific capacitance of hundreds of $\mu\text{F}/\text{cm}^2$. It has been reported that the double layer capacitance of activated carbon was about 15-20 $\mu\text{F}/\text{cm}^2$.¹⁶ The specific capacitance of electrolyte supercapacitors using porous rGO electrodes is normally in the range of 200- 400 $\mu\text{F}/\text{cm}^2$.⁵ The relatively high capacitance of D2 indicates high dielectric constant of the GO film. Supposing a double layer capacitor with two parallel Au films with interdistance of 400 nm and without any filler in the gap, the capacitance per unit area is given by $C/A = \epsilon_0/d$, as 0.022 $\mu\text{F}/\text{cm}^2$, where A is the area, d is the gap between the metal electrodes, and ϵ_0 is the vacuum permittivity. We treat the D2 device as an ideal capacitor to calculate the capacitance by using the imaginary part of impedance, $Z(\text{Im})$, as $C = -1/2\pi fZ(\text{Im})$. According to this equation the capacitance versus frequency is plotted in Fig.4(b). In **Figure 5.4 (a)**, the capacitance of D2 decreases from 512 $\mu\text{F}/\text{cm}^2$ to 167 $\mu\text{F}/\text{cm}^2$ with the voltage scan rate increasing from 10 mV/s to 500 mV/s . In **Figure 5.4 (b)**, the capacitance of D2 is in the order of 10² $\mu\text{F}/\text{cm}^2$ if the AC frequency is below 0.67 Hz. The dielectric constant of the GO film against frequency can be deduced by $\epsilon_r = Cd/A\epsilon_0$, and the curve is plotted in **Figure 5.4 (b)**.

It is surprising to see that the relative permittivity of GO is in the order of 10^4 when the AC frequency is below 75 Hz. Kou *et al* investigated the dielectric performance of a GO/polyamide composite. At 100 Hz the ϵ_r of polyamide is ~ 3 but it increased up to ~ 1000 if doped with 1 wt% GO.¹⁷ The ϵ_r of GO film measured from our D2 device with an Au/GO/Au capacitor structure confirms that GO can be used as a high dielectric material, which may be used for capacitive energy storage.

5.6 Conclusions

In summary, solid state thin film capacitors were made by using wet-chemically produced GO and electrochemically exfoliated graphene. Two prototype devices, D1 and D2, with a G(25 nm)/GO(350 nm)/G(25 nm) stacked film and a sole 400-nm-thick GO film, respectively, as spacer between two opposite Au films were used to study the effect of graphene electrode and GO dielectric spacer on the capacitive performances. By comparing the two devices, we found that the use of graphene film electrode can increase the capacitance about two times. The capacitance of devices with GO film spacer decreases with increasing the voltage scan rate or the AC frequency. High capacitance of $1410 \mu\text{F}/\text{cm}^2$ was achieved from the D2 device with voltage scan rate of 10 mV/s. The D2 device with Au/GO/Au structure has capacitance order of $10^2 \mu\text{F}/\text{cm}^2$ which is also comparable to that of graphene-based electrolyte supercapacitor, owing to the high dielectric constant of GO film. We deduced that in the frequency range of 0.5-70 Hz, the relative permittivity of GO film is in the order of 10^4 . Our study suggests that the electrochemically-exfoliated graphene can be a good electrode material for supercapacitors, while the highly-resistive GO, which can be large-scale produced by the wet-chemical method, has very high dielectric constant and can be applied as spacer in thin-film supercapacitors.

5.7 Acknowledgement

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6 Highly NO₂ Sensitive Caesium Doped Graphene Oxide Conductometric Sensors

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6.1 Prelude

The industrial development in the last decades together with the drastic improvement of quality of life and the massive employment of cars producing harmful gases such as CO, NO, NO₂, SO₂ etc., has increased the needs for quantitative detection of different analytes and air-quality monitoring.

Metal oxide based gas sensors have been developed, based on their ability of change in the electrical conductivity with the adsorption and desorption of gases at high temperatures. Several metal oxides such as ZnO, SnO₂, CdO etc., were investigated and shown high sensitivity. However, they had poor long-term stability.

Carbon based nanomaterials such as graphene, carbon nanotubes etc., have been attracting ideal components as gas sensors due to their excellent detection sensitivity and long-term stability arisen from high specific surface area and quasi-one dimensional materials properties. The sensitivity and selectivity of carbon nanomaterials can be engineered by employing different techniques, for example: create defects and graft functional groups to their surface. It has been reported that gas sensing performance of reduced GO is superior to that of pristine graphene and it can be further enhanced by doping with alkali metals.

In this paper, we reported for the first time, gas sensing performance of a caesium-doped GO (Cs-GO) based conductometric sensor for NO₂ detection.

6.2 Statement of Contribution

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of the journals or other publications and (c) the head of the responsible academic unit, and
5. they agree to the use of publication in the student's thesis and its publication on the Australia Thesis Database consistent with any limitation set by publisher requirements.

In the case of this chapter:

Highly NO₂ sensitive caesium doped graphene oxide conductometric sensors

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Contributor	Statement of contribution
Carlo Piloto	Fabrication and characterization of gas sensors, data analysis, paper writing
Marco Notarianni	data analysis, paper writing
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Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

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16/6/15

Name

Signature

Date

Abstract

Here we report on the synthesis of caesium doped graphene oxide (GO-Cs) and its application to the development of a novel NO₂ gas sensor. The GO, synthesized by oxidation of graphite through chemical treatment, was doped with Cs by thermal solid-state reaction. The samples, dispersed in DI water by sonication, have been drop-casted on standard interdigitated Pt electrodes. The response of both pristine and Cs doped GO to NO₂ at room temperature is studied by varying the gas concentration. The developed GO-Cs sensor shows a higher response to NO₂ than the pristine GO based sensor due to the oxygen functional groups. The detection limit measured with GO-Cs sensor is ~90 ppb.

Keywords: *Gas sensor, Nitrogen dioxide, Caesium, Drop casting, Graphene oxide, Highly sensitive, Conductometric, Doping*

6.3 Introduction

Graphene is a single layer of carbon atoms arranged in a honeycomb lattice.¹⁻² Intrinsic low noise structure, large specific surface area and extraordinary mobility of carriers are the unique properties that make graphene-based materials excellent candidates for a wide variety of electrical applications.³ One of the most promising applications is chemical sensing with detection limit down to ppb level.⁴⁻¹¹ Such ultrahigh sensitivity can play a crucial role in applications including health care, gas alarms, safety and environmental monitoring.¹²

Theoretical¹³⁻¹⁴ and experimental¹⁵⁻¹⁹ studies have revealed that functionalization of graphene can improve significantly its gas sensing performance.²⁰ The presence of dopants or defects in the graphene lattice can increase the adsorption energy, i.e. the gas molecules can absorb more strongly on the doped or defective graphene than the pristine graphene resulting in an enhancement of the sensitivity or selectivity.

Recently, graphene oxide (GO), a graphene layer decorated with oxygen functional groups, has been subject to extensive research^{7, 21-24}, as the synthesis of GO is the first step to easily obtain functionalized graphene.²⁵ GO can be synthesized from colloidal suspensions of graphite derivatives²⁶⁻²⁹, e.g. graphite oxide, a method significantly cheaper and scalable than most of the common processes to make

pristine graphene sheets, like chemical vapour deposition, epitaxial growth or mechanical exfoliation.^{12, 30-32}

By dispersion and sonication of graphite oxide in aqueous solution or organic solvent, a colloidal suspension of GO sheets is produced. The density of oxygen functional groups can be easily controlled^{26, 33-37} making this process a good candidate for graphene functionalization. The oxygen groups of the resulting GO lead to the disruption of the graphitic structure, thus making the material electrically too much insulating for resistive gas sensing applications. However, the partial removal of oxygen groups, leading to reduced GO can be achieved by chemical^{34, 38}, thermal³⁹⁻⁴⁰ or ultraviolet-assisted process⁴¹. The conductivity and gas sensing performance of the reduced GO is comparable or superior to that of the pristine graphene⁴², due to the oxygen defects that act as low energy adsorption sites.

To further enhance its gas sensing properties, reduced GO can be doped with alkali-metals¹⁸, similarly to what has been done in other carbon materials, to tune up the electronic properties for sensing applications⁴³.

Different research groups have reported high gas sensing performance of conductometric devices based on GO^{25, 36, 44}, reduced GO (rGO)^{16, 22, 24, 28, 45-46} and functionalized rGO^{18, 47-49}. Prezioso et al.²⁵ have measured the NO₂ sensing performance of GO drop casted on standard interdigitated Pt electrodes. They reported a very low detection limit (20 ppb), which is attributed to the high quality of their GO samples (large and highly oxidized flakes). Robinson et al.⁴⁵ demonstrated that by increasing the level of reduction it is possible to improve the response time and 1/f noise. It has also been proven by Yuan et al.⁴⁷ that reducing the thickness of the sensing layer below 5 nm results in a significant enhancement of the sensitivity⁴⁷; although other authors claim that very thin layers would result in a not uniform conducting path¹⁸. The decoration of rGO with Pd nanoparticles using sputtering or by alternating current dielectrophoresis has shown an improvement in the sensitivity to NO by a factor of 5 (down to 2 ppb at room temperature)¹⁶ as well as selectivity to hydrogen¹⁸.

Increasing air pollution and global warming raised the demand for highly sensitive and portable NO₂ gas sensors. To this purpose, metal-oxide materials have been investigated reaching the lowest detection threshold of 0.1 ppm.⁵⁰ The high operating temperature of these devices, in the range of 200-400 °C, is a serious

drawback that makes difficult their utilization in the field, where power consumption is a critical parameter. Carbon-based materials, such as graphene and chemically derived graphene, offer high sensitivity to cost ratio even when operating at room temperature.⁵¹

In this article, we report for the first time the fabrication, characterization and gas sensing performance of a caesium-doped GO (GO-Cs) based conductometric sensor. Due to the reported catalytic activity of Cs, we believe that the sensing performance of the GO can be improved significantly.⁵² Both pristine GO and Cs doped GO sensors have been tested towards different concentrations of NO₂ gas at room temperature. The detection limit measured with GO-Cs sensor is ~90 ppb.

6.4 Experimental

6.4.1 Device fabrication

GO materials were prepared by oxidation of graphite flakes following the method reported by Marcano et al.⁵³ Commercially available graphite flake was purchased from Sigma Aldrich. All other chemical used, (99.99% H₂SO₄, 85% H₃PO₄, 35% HCl, 30% H₂O₂, KMnO₄) in this study were analytical grade and supplied by Sigma Aldrich. Analytical grade Ethanol, Acetone and Diethyl ether were used as solvents.

The graphite mixed with KMnO₄ (ratio of 1:6) was combined with a mixture of H₂SO₄:H₃PO₄ (540:60 mL) acids. The reaction was stirred at 50°C for 12h. Subsequently, the resulting mixture, cooled at room temperature, was poured onto ice with 3ml of 30% H₂O₂ and sifted through a 250µm sieve. The filtrate was centrifuged at 4000rpm for 30min. The obtained material was washed with DI water, HCl and ethanol. After each wash, the mixture was sieved and centrifuged for 30min at 4000rpm. The final precipitate was coagulated with diethylether. Coagulated solid was dissolved in DI water and sonicated for 1 h. The resulting GO aqueous dispersion was cooled down for 24h followed in a de-freezer and subsequently for 72h in a freezer dryer at -51°C under vacuum.

In order to synthesize GO doped with caesium (GO-Cs), the GO was diluted in water and mixed with Cs₂CO₃, following the method suggested by Liu et al.⁵⁴ The obtained solution was stirred at room temperature for 30 min and sieved with a

polyvinylidene fluoride membrane (0.2μm). The precipitate was then added to water (30mL) and filtered. The process was repeated twice to obtain dark solid GO-Cs.

Finally, the gas sensors were fabricated by drop casting of the prepared GO and GO-Cs materials onto 2×2 mm² transducers and then they were placed in oven at 60°C for 12h. The transducers consisted of Pt interdigitated electrodes (IDT) (200μm separation) deposited on 0.25mm thick alumina substrates.

6.4.2 Material characterisations

The structure and the composition of the synthesized GO and GO-Cs was analysed by field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Raman spectroscopy and Kelvin probe force microscopy (KPFM).

XPS data were acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165mm hemispherical electron energy analyser. The incident radiation was Monochromatic Al K α X-rays (1486.6eV) at 225W (15kV, 15ma). Survey (wide) scans were taken at analyser pass energy of 160eV and multiplex (narrow) high resolution scans at 20eV. Survey scans were carried out over 1200-0 eV binding energy range with 1.0eV steps and a dwell time of 100ms.

Narrow high-resolution scans were run with 0.05eV steps and 250ms dwell time. Base pressure in the analysis chamber was kept at 1.0x10⁻⁹ torr and during sample analysis 1.0x10⁻⁸ torr. Peak fitting of the high-resolution data was also carried out using the CasaXPS software.

Raman spectroscopy was performed by using an “inVia Renishaw Raman microscope” with $\lambda = 532$ nm operated at 35 mW, with a 1μm spot size, to investigate bond changes and defects in the material.

The KPFM was performed with a commercial AFM (Cypher-Asylum Research) equipped with an air temperature controller (ATC). The ATC flows temperature regulated, HEPA (High-Efficiency Particulate Absorption) filtered air through the Cypher enclosure. Closed-loop temperature control isolates the AFM from room temperature variations, minimizing thermal drift for imaging. During measurements the temperature was kept constant at 26°C.

For all KPFM data shown here, we used conductive (Pt coated) AFM probes (NSG03 model from NT-MDT) with a nominal resonant frequency between 50 and

150kHz. The GO and GO-Cs samples were deposited on gold-coated mica substrates from a liquid suspension (5 μ g/mL). The Kelvin voltage was maintained with an integral gain of 4, no proportional gain, and an AC-voltage applied to the tip of 3V.

6.4.3 Gas sensing measurements

The GO and GO-Cs sensors response to NO₂ was evaluated using a high precision multi-channel gas testing system, including a 1100cc volume test chamber capable of testing four sensors in parallel, 8 high precision mass flow controllers (MKS 1479A) to regulate the gas mixture, 8-channel MFC processing unit (MKS 647C), a picoammeter (Keithley 6487) and a climatic chamber to control the temperature. The measurements were performed at room temperature with a mixture of synthetic air and NO₂ gas in different concentrations (up to a maximum of 12.2ppm of NO₂ balanced in synthetic air). The right concentration of NO₂ gas in air was obtained by adjusting the respective flow rates via the MFCs, while maintaining a total constant flow rate of 200SCCM (mL/min). The response upon gas exposure was evaluated by measuring the sensors resistance variation with bias voltage of 3V.

6.5 Results and discussion

6.5.1 Material characterisations

The morphology of the synthesized graphite oxide powder was investigated by FESEM (**Figure 6.1**). It is evident that the thin and aggregated flakes are stacked to each other with lateral sizes ranging from several hundred nanometers to several microns.

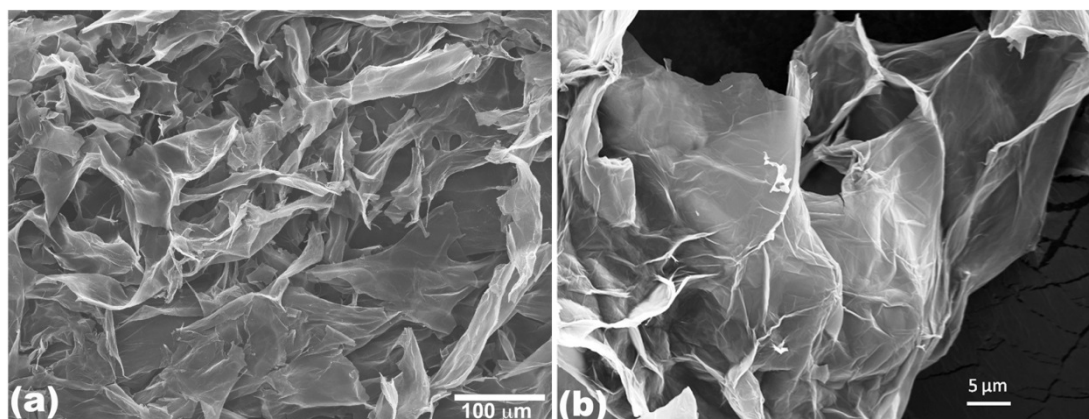


Figure 6.1.(a) Low magnification and (b) high magnification SEM images of graphite oxide flakes.

AFM images (**Figure 6.2 (a)** and **(c)**) confirm that most of GO and GO-Cs flakes are ~ 1 nm thick, corresponding to one monolayer, with a lateral size in the range of hundred nanometers.⁵⁵⁻⁵⁶ The thickness of each GO layer is usually higher than the pristine graphene sheet because of the orthogonally bonded oxygen groups coming out from the surface.^{26, 56-57}

Electrical characterizations were carried out with KPFM providing a potential map of the samples with a resolution of few mV. **Figure 6.2 (b)** and **(d)** show a comparison of pristine GO and GO-Cs KPFM signals.

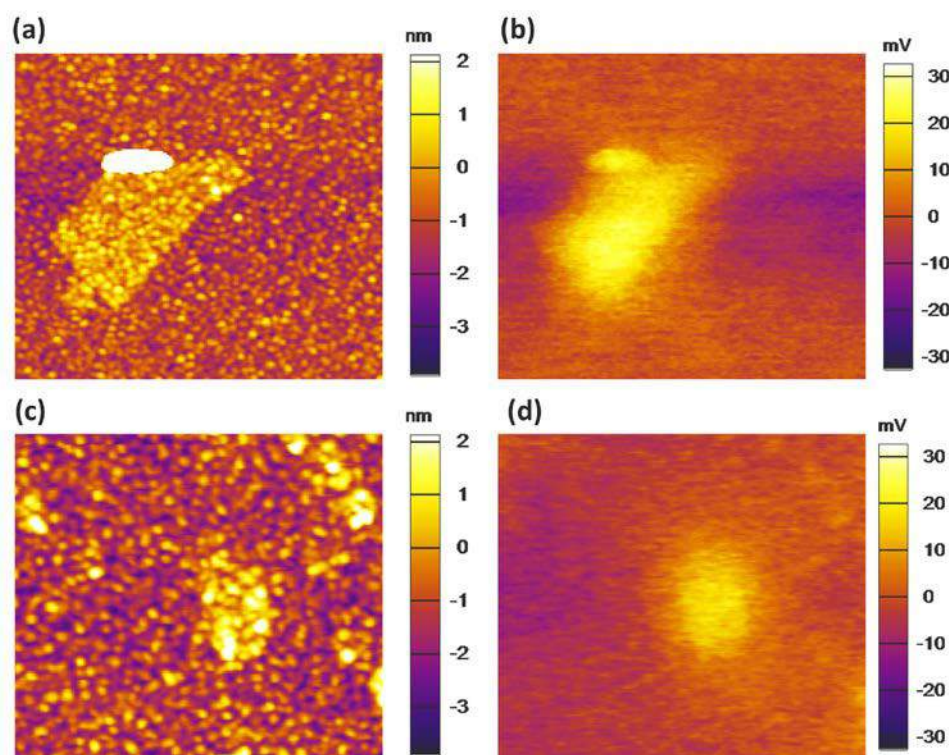


Figure 6.2. AFM and KPFM images of (a) and (b) a GO flake (2x2 nm); (c) and (d) a GO-Cs flake (1.4x1.4 nm).

The measurements collected from several samples and on different flakes show a net difference in the potential map of GO (see **Figure 6.2 (b)**) and GO-Cs flakes (see **Figure 6.2 (d)**), with a drop of the average potential on a flake from $30 \text{ mV} \pm 3 \text{ mV}$ in the GO to $19 \text{ mV} \pm 3 \text{ mV}$ in the GO-Cs. We attribute this drop to the chemical reduction of the GO caused by the Cs_2CO_3 that tends to decrease the work function as observed by^{54, 58-60}. This result suggests that doped GO may have good performance as a gas sensing material.

XPS survey analysis of the GO (**Figure 6.3 (a)** blue line) confirms that the GO does not contain any contaminants and is largely oxidised with an oxygen content of

~32%. A reduction of the oxygen content down to ~ 24% is observed in the GO-Cs (Figure 6.3 (a) red line) survey spectrum, which confirm the presence of ~5% Cs. In the high resolution XPS spectra of the C peaks (Figure 6.3 (b) and (c)), we identify the C-C contribution as the peak at 285.3 eV binding energy, while the C-O, C=O and COOH groups are assigned to binding energies of 287.5, 288.4 and 289.1 eV, respectively.⁶¹⁻⁶² Figure 6.3 (b) and (c) show that the intensity of the C-O band in the GO-Cs decreases compared to the C-O band of the GO, confirming a reduction mechanism occurring in the GO due to the Cs_2CO_3 . Also the COOH peak decreases appreciably in the GO-Cs because of the substitution occurring between -COOH (that are usually at the periphery in the GO flakes), with -COOCs groups.⁵⁴ During the reaction, Cs^+ is in fact expected to replace the H^+ ions in COOH groups due to its higher reactivity. This is confirmed by the position of the Cs 3d5/2 peak at 724.1 eV (high resolution data, not shown), corresponding to the value of Cs bound to a carboxylic group.⁵⁴ It is worth also to notice the effect of the doping on the Fermi level, causing a 1 eV shift towards lower binding energy of all C peaks in the XPS spectra of GO-Cs (Figure 6.3 (c)). The edge functionalization with the introduction of Cs^+ does not cause much change in the carbon skeletons of the graphene oxide as observed by Liu et al.⁵⁴ and confirmed by our Raman spectra of GO and GO-Cs (Figure 6.4), where no appreciable shift is found in the D and G peaks. The 2D peak does not change as well, while the shape is compatible with the presence of several layers in the GO flakes. However a net increase in the D peak at 1360 cm^{-1} of the GO-Cs sample is a signature of the increased number of defects due to the presence of Cs^+ .

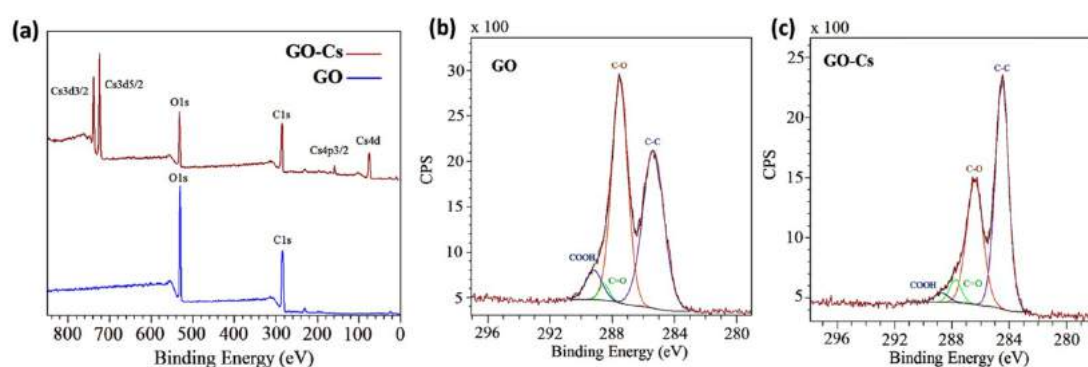


Figure 6.3. (a) XPS survey spectrum of GO (blue line) and GO-Cs (red line); High resolution XPS C1s spectra of (b) GO and (c) GO-Cs. The ~ 1eV shift towards lower binding energy of the peaks in (c) is due to the shift of the Fermi level caused by the doping.

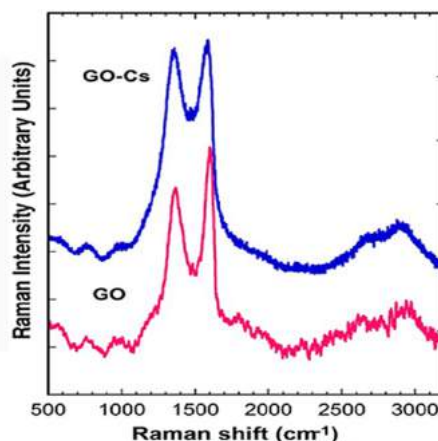


Figure 6.4. Raman spectra of GO-Cs and GO, displaying intense D and G peaks at ~ 1380 and ~ 1600 cm^{-1} , respectively. The increase of the D peak, which is the signature of defects in graphene and GO, is clearly linked to the presence of Cs in GO-Cs.

6.5.2 Gas sensing performance

The GO-Cs and pure GO sensors were tested towards different concentrations of NO₂ gas balanced in synthetic air at room temperature. The sensors response (R) was calculated according to the equation:

$$R(\%) = 100 \times \frac{(R_{\text{air}} - R_{\text{gas}})}{R_{\text{air}}} = 100 \times \frac{\Delta R}{R_{\text{air}}} \quad (16)$$

where; R_{air} is the sensing film resistance under synthetic air only and R_{gas} is the film resistance during NO₂ exposure.

As expected, the GO film showed a much higher resistivity than the GO-Cs film in the presence of air (1013 Ω vs. 1010 Ω). The lower baseline resistance can be attributed to the reduction of oxygen groups in GO-Cs film as confirmed by XPS analysis (**Figure 6.3**). Being the value close to the resolution capability of our source meter (10fA), the measurements of the GO film was affected by electrical noise.

We studied the response at room temperature towards different concentrations of NO₂, ranging from 0.090 to 12.2 ppm. Both sensors exhibited a reduction in resistivity upon exposure to the gas, in agreement with the theory developed by Tang and Cao¹⁴: a negative charge is transferred to the NO₂ molecules, mostly in correspondence of oxygen functional group, resulting in a p-type behaviour, which was also observed by Prezioso et al.²⁵ For NO₂ concentrations higher than 3 ppm both GO and GO-Cs exhibited a significant response, while at low concentrations the GO-Cs performed better. The GO-Cs sensor exhibited a significant response to NO₂, down to

concentrations as low as ~ 91 ppb, while GO sensor did not show any response to concentrations below 3ppm. This sensitivity enhancement could be attributed to defects introduced into the GO-Cs films during the doping process. **Figure 6.5** shows the plot of the GO and GO-Cs sensors response as a function of NO_2 concentration. Both responses are approximately linear and proportional to the gas concentration. Since NO_2 is an oxidative gas with strong electron-withdrawing ability, the decrease in resistance confirms the p-type semiconductor behaviour of the sensors, like the one observed for carbon nanotubes.⁶³ For GO-Cs sensor a relative increase in the response (RGO-Cs) of 0.7, 1, 2, 4.4, 10, 24 and 40% was recorded for 0.18, 0.36, 0.73, 1.5, 3, 6.1 and 12.2ppm NO_2 , respectively. Even at very low gas concentrations, a slope of about 3% ppm can be observed (inset of **Figure 6.5**), confirming that the as-prepared GO-Cs sample is highly sensitive to NO_2 . On the contrary, no appreciable response has been recorded for GO sensor in the presence of concentrations below 3ppm, while a relative increase in the response (RGO) of 18, 41, 65% was recorded for 3, 6.1 and 12.2ppm NO_2 , respectively. **Table 6.1** summarises the response of the GO and GO-Cs sensors for comparison.

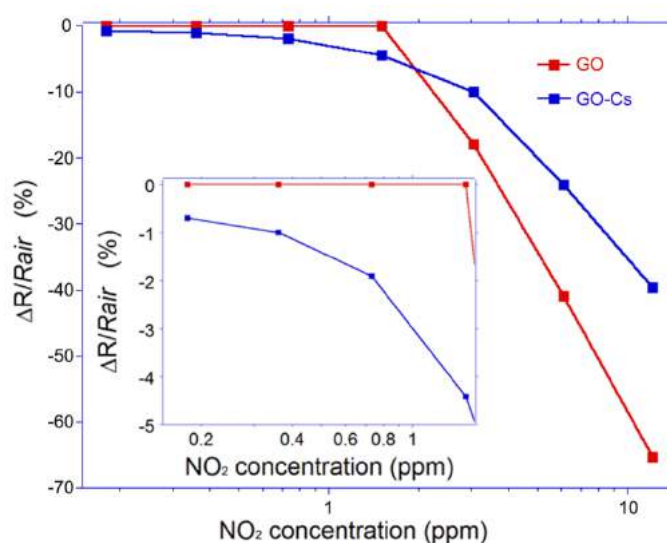


Figure 6.5. Response of the GO and GO-Cs based sensors as a function of NO_2 concentration. The inset shows the response at very low concentrations.

We observed that the resistance of both sensors kept on decreasing even after 20 min exposure to NO_2 , reaching very slowly the saturation state. From deep saturation, the film required a very long time exposure to dry air to recover its original value. However, the significant variation of the resistance during the first

phase of exposure can ensure a successful employment on the field of the sensing device. Therefore, we consider the exposure of approximately 4 min as an effective response time. This value has been chosen also in consideration of the time required to fill the volume of the gas chamber (1100cc) with the target gas, which affects the dynamic response. The dynamic responses of GO and GO-Cs upon 4 min exposure to NO₂ concentrations decreasing from 12.2 to 1.5ppm have been measured simultaneously.

Table 6.1. Comparison of the GO and GO-Cs response towards NO₂ with different concentrations.

NO ₂ [ppm]	R _{GO} [%]	R _{GO-Cs} [%]
0.18	-	0.7
0.36	-	1
0.73	-	2
1.5	-	4.4
3	18	10
6.1	41	24
12.2	65	39.6

As it can be seen from **Figure 6.6 (a)**, the GO response is initially higher than GO-Cs, but decreases more rapidly. When exposed to 1.5ppm, GO response is not anymore appreciable while a GO-Cs reaction is still evident. The noisier curves of GO is due to its higher resistivity value. Both sensors exhibit a long time to recover their initial value. Approximately 220 minutes are needed, although this value may be affected by the presence of residual NO₂ molecules present in the 1100c gas chamber. While GO sensor recovers faster, GO-Cs is not able to fully recover its initial baseline. The dynamic response of the GO-Cs sensor upon 4 min exposure to 0.091, 0.18, 0.36, 0.732 and 1.44ppm NO₂ are shown in **Figure 6.6 (b)**. The GO-Cs sensor reacts after few tens of seconds to the NO₂ even at very low concentrations, down to 180 ppb. In terms of recovery time, for concentrations below 1ppm, few minute exposures to dry air is enough to restore the original resistivity value. For higher concentrations, the recovery is longer, suggesting that the amount of Cs doping can be optimized to make a balance between the sensitivity and recovery time. This is in agreement with what observed by other researchers.^{25, 45} As shown in **Figure 6.6 (c)**, the GO-Cs sensor exhibits a good repeatability, even if a slight drift in the baseline is observed. This may be due to the presence of gas molecules not yet desorbed from the

sensor surface. An average time of 540 sec is needed to recover after 240 sec 0.732ppm NO₂ exposure.

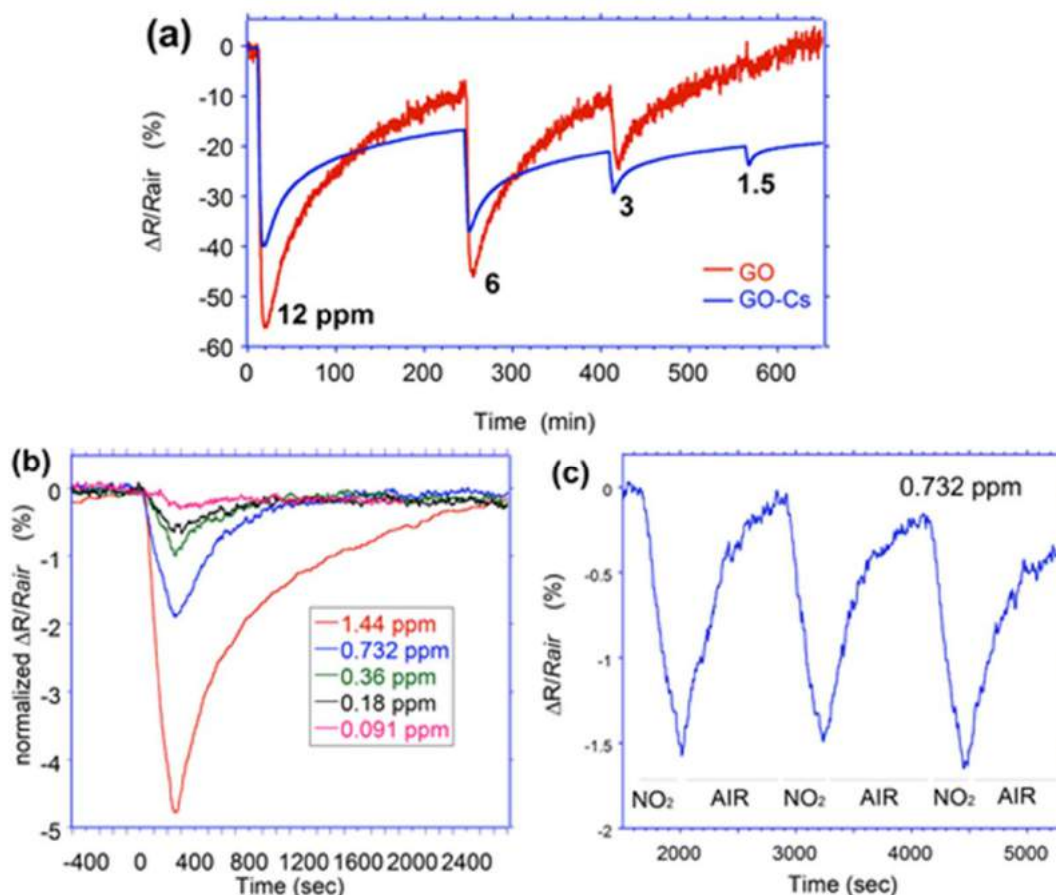


Figure 6.6. Response of (a) GO-Cs and GO based sensors towards NO₂ with concentrations higher than 1 ppm; (b) GO-Cs based gas sensor after exposure to different concentrations of NO₂ ranging from 0.091 to 1.44ppm and (c) GO-Cs based sensor during 3 successive cycles of exposure to 0.732ppm NO₂ for 4 min and to dry air for 15 min.

6.6 Conclusions

We successfully fabricated and studied for the first time an NO₂ sensor based on caesium-doped graphene-oxide (GO-Cs). We demonstrated that caesium doping is an effective technique to reduce the GO, making it a promising material for gas sensing applications. XPS, Raman and KPFM results confirm the successful incorporation of Cs into the GO resulting in the reduction of oxygen groups. The developed GO-Cs based conductometric sensor exhibits a very low detection limit for NO₂ (down to ~90ppb) at room temperature. This can be attributed to the p-character of the GO film, due to the intercalation of Cs atoms leading to the reduction of oxygen groups.

However, the sensor shows very long recovery, making GO-Cs a good candidate for applications requiring high sensitivities, but not fast response. Future works will focus on investigating the effect of different species and concentration of dopants on improving the selectivity, response and recovery time.

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7 Conclusions and Future Directions

Graphene and its derivatives are important in several fields of applications including polymer composites, electronics, energy storage, chemical sensors etc. However, there are still many challenges and issues to overcome in order to realize the full potential of these materials in these applications. In graphene-polymer nanocomposites, a better understanding of microchemical and micromechanical behaviour at the interphase between graphene and polymer matrix is utmost important to obtain desirable final properties. This thesis explored the chemical nature and mechanical behaviour of the interphase of graphene oxide-epoxy nanocomposites. In particular, the impact of loading content and microchemical environment of graphene oxide on reinforcement, toughening mechanisms and cure chemistry of epoxy resin was investigated.

GO was synthesised following the modified Hummers method. The perfect formation of GO structure was evidenced by spectroscopic and microscopic data including TEM, AFM, XPS, and Raman etc. GO can completely be dispersed in several organic solvents including DMF and water by simple ultrasonication process.

GO-epoxy nanocomposites were fabricated based on solution mixing technique which produced nanocomposites with homogeneously dispersed GO in the epoxy matrix, evidenced by Raman mapping and TEM. The nanocomposites exhibited significant enhancement in mechanical properties, particularly fracture toughness (K_{Ic}) at very low loading of GO. Significant improvement in properties can be attributed to several reasons, such as high surface area with two dimensional geometry, wrinkled surface topography, as well as uniform distribution and strong interactions between GO and the matrix. However, we found that achieving a uniform dispersion of GO was challenging especially at higher loadings. It was seen that for higher GO loading, the enhancement ability of GO in mechanical properties became weaker. This decrease could be a result of degradation of the dispersion quality of GO at higher loading fractions as observed in Raman mapping and TEM. Crack deflection is the main mechanism responsible for toughening in GO epoxy nanocomposites. DSC data further confirmed the higher toughness of epoxy matrix in nanocomposites, demonstrating that decrease in T_g of epoxy matrix with GO incorporation.

Kinetic study of epoxy nanocomposites with 0.3 wt% GO was carried out by FT-IES method. This special technique offered *in situ* monitoring of curing process in real time at the interphase region of GO and epoxy. Comparison study of as produced GO (aGO) and OD free GO (acGO) showed the hindrance effect of aGO on epoxy cure. Interestingly, it has been noticed that removal of OD switched the hindrance effect to a catalytic effect. Moreover, OD itself could stimulate the homopolymerization of epoxy by catalysing epoxide ring opening reaction. Therefore, both retardation behaviour and homopolymerization in aGO nanocomposite resulted in lower crosslinking density at the aGO-epoxy interphase thus producing a lower T_g and higher toughness. DSC further confirmed the retardant and catalytic behaviour of GO with OD and without OD, respectively, where the presence of OD on aGO leads to slower conversion of cure reaction in epoxy matrix and decreased cross-linking density. Strongly adhered OD was found to have covered the available reactive sites which are responsible for the acceleration of cure process. Therefore, our study revealed that small addition of as produced GO can effectively improve the toughness of epoxy matrix.

GO is not only a suitable candidate for polymer composites but also other applications such as in electronic devices, solar cells, gas sensors, energy storage etc. This thesis attempted fabricating thin film capacitors using GO as dielectric spacer and electrochemically exfoliated graphene as electrodes. The devices exhibited high capacitance due to high dielectric constant and electrical resistivity of GO. Further, it has been shown that graphene can be used as sensing material and sensitivity and selectivity of graphene could be engineered by introducing dopants or defects. Our experimental data reveals that doping of GO with Cs_2CO_3 (GO-Cs) can significantly enhance the sensitivity of graphene for NO_2 gas at room temperature. The GO-Cs sensor exhibited a significant response to NO_2 , down to concentrations as low as ~91 ppb as well as a good repeatability compared to GO sensors. The sensitivity enhancement in GO-Cs was found to be due to an increase of defects sites in GO-Cs films during the doping process.

It is apparent from our study that as-produced GO can effectively enhance the mechanical properties of epoxy resins, especially fracture toughness. IR emission results suggest that GO significantly change the cure kinetic at the interphase region consequently changing both crosslinking density and toughness of the epoxy matrix.

The potential applications of GO for energy storage and gas sensing applications were also explored.

Throughout this thesis it has been demonstrated that GO has some remarkable features that are attracting for several applications. Future work on GO should focus on:

- Isolation of OD by autoclaving should be more widely investigated for better understanding of its structure as well as characteristic properties. It is also important to discover how to recombine these separated OD and GO in order to realize chemical interactions between two materials and revert back to original properties such as dispersion, fluorescence properties etc. Similarly, characterization of OD-free GO should be important in electrical and thermal conductive properties.
- In this work, we investigated how OD-free GO affected the cure process and chemical reactions at the interphase of GO and epoxy matrix. However, its effect on overall performance of different polymer matrices including epoxy needs to be more widely investigated.
- GO modification with different dopants and surface functional groups and evaluation of property changes in GO to expand the application of GO in sensing and energy storage devices are important.
- GO quantum dots are another emerging field to discover especially for the use of them in capacitors and solar cells.