

Literature study of graphene modified polymeric composites

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Summary

This study presents a survey of literatures including recent work in relevant projects, on graphene modified polymeric composites with a particular focus on fibre reinforced polymeric composites.

A variety of routes that are used and can potentially be used to integrate graphene into composites are reviewed, including dispersing graphene into a polymer matrix, doping graphene onto fibre reinforcement, graphene modified prepreg and the use of graphene buckypaper. The effect of processing parameters, such as dispersion and doping methods, temperature, pressure, etc., along with modification of graphene, on the structure and mechanical, electrical, thermal, barrier, rheological and crystalline properties of the resultant composites are also reviewed.

The most prominent influencing factors are the intrinsic properties of graphene including aspect ratio of nanoplatelets and surface functionalization, dispersion and exfoliation as well as orientation and alignment of graphene, and interactions of graphene-polymer and graphene-fibre reinforcement. The selection of processing techniques and tailoring of influencing factors depend on the required properties. For instance, deposited graphene onto fibres for reinforcement can be more efficient than dispersed graphene into the polymer to improve the interfacial and interlaminar properties. Well-dispersed and randomly oriented graphene can be more beneficial than well-dispersed and aligned graphene for higher electrical conductivity while less favoured for higher mechanical properties. Potential applications of graphene modified polymeric composites addressing industrial and societal challenges are also discussed.

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1. Background of this literature study

Soon after Kostya Novoselov and Andre Geim (University of Manchester) discovered the 'wonder material' graphene, researchers started using it in various areas in the hope of converting its astonishing properties into disruptive technologies. The publication trend (total articles retrieved via Web of Science search tool) reveals that the amount of research on graphene has increased exponentially from 90 articles in the year 2000 to 44,648 articles in the year 2015. Graphene has become a primary research focus in many current fields of science. This can be evidenced by the announcement by the European Commission in 2013 of €I billion for funding the Graphene Flagship, a Future and Emerging Technologies (FET) Flagship, for the commercialisation of graphene research over ten years (press release on 2013-01-28)¹. The Graphene Flagship is the EU's biggest ever research initiative, tasked with bridging together academic and industrial researchers to take graphene from the realm of academic laboratories into European society in the space of ten years, thus generating economic growth, new jobs and new opportunities.

"The first experiments with graphene composites occurred in 2006, but the research is still in an early phase", said engineer Andrea Ferrari, Director of Britain's Cambridge Graphene Centre and Chair of the Graphene Flagship's Executive Board. Many fundamental issues still need to be addressed such as processing routes and orientation, but the initial niche applications are appearing. "For example, a line of Head tennis rackets that are made of graphene composites is being used by Novak Djokovic and Maria Sharapova."

One of the most likely direct and prominent applications of graphene-based products is for advanced composite materials. Thanks to the anticipated future demand for lightweight vehicles, the automotive industry is expected to be the highest user of advanced composite materials by volume, said Ahmed Elmarakbi, a professor of Automotive Engineering at the University of Sunderland in the UK, Founding Editor-in-Chief of the International Journal of Automotive Composites, and a Member of the EU Graphene Flagship. Figure 1 shows how Fiat researchers see numerous potential automotive applications for graphene.



Figure 1: Lightweight graphene based components by Fiat²

While graphene is in the long term expected to offer a wide number of solutions for various industrial sectors, numerous challenges have to be overcome even in developing a fundamental understanding of graphene-based materials and their polymeric composites. Some commonly recognized challenges are listed as per below³:

- Lack of new methods for large-scale production of graphene-based products especially customized products
- The modification efficiency in composites is still far below the expectations, based on the outstanding properties of graphene the improvement of strength, stiffness and toughness, etc., is insufficient
- No existing materials model, on commercial explicit finite element software, to model graphene modified composite materials for high performance structural applications
- Lack of knowledge on graphene composites for high performance structural applications and interface properties between the graphene and polymer matrix under severe loading conditions, such as fragmentation and crash
- Lack of knowledge on designing graphene composites structures that can offer high stiffness, strength as well as predictable and safe failure modes
- The joining of dissimilar materials is not covered by an appropriate know-how and several critical points are not yet solved by the scientific community and researchers.

Most of the articles and reports on graphene modified composites have been made at lab scale. Among these studies, graphene modified polymer (GMP) composites occupy the vast majority, leading to a number of review articles. GMPs can be used solely as nanocomposite (only with nano-scale reinforcement) materials which have shown great potential in particular applications for electronic devices, field effect transistors, solar cells, energy storage devices, and in an emerging direction of biomedical applications. They can also be used as advanced matrix, which can improve the bulk properties especially those of polymer-rich regions and introduce new functions, such as electrical, thermal and shielding, in composites having reinforcement at other scales, such as fibre reinforced polymer (FRP) composites. FRP composites are widely used in automotive, aerospace and aeronautics, defence, construction, marine and sport owing to their high strength to weight ratio, excellent fatigue and corrosion resistance, etc. The use of novel graphene technologies will benefit the development of advanced FRP composites which are of lighter weight, higher performance and more functionalities relative to traditional FRP composites. GMP is one of the most important resources for advanced FRP composites, nevertheless, it is not the only method. Graphene can also be integrated into FRP composites by, for instance being doped on fibre reinforcement, or inserted/coated as large-area layers, based on the modification purpose/targets. Studies that summarize the technologies of processing, characterization, and modeling of graphene modified FRP (GMFRP) composites, are in great need for both academia and industri but very lack of in the current stage.

This study hence aims to perform a review to update the technical development of graphene modified polymeric composites– processing, characterization, modeling and commercialization, in order to upgrade laboratory results to pratical applications.

2. Graphene modified polymeric composites

2.1. Composites based on graphene modified polymers (GMPs)

The integration of nanomaterials in a polymer matrix has opened up a new and interesting area in materials science in recent years. These materials show considerable improvement in properties that cannot normally be achieved using conventional composites or neat polymers. The property enhancements correlate strongly with nanocomposite microstructure, which depends significantly upon the affinity between phases and processing techniques. Graphene/polymer nanocomposites, thermoplastic- and thermoset-based, have three morphological states similar to layered silicate nanocomposites: phase separated (microcomposite), intercalated (nanocomposite) and exfoliated (nanocomposite). When good dispersion and sufficient exfoliation is achieved, property improvements will be obtained at very low filler loadings in the polymer matrix. Immiscibility of the phases and/or insufficient exfoliation of graphene prior to mixing with polymer can result in large agglomerates even when single-layer graphene is used.

2.1.1. Processing methods and efficiency

There are most commonly three methods to prepare GMPs: in situ polymerization, solution (or solvent) mixing and melt compounding.

In situ polymerization is a method which has been used successfully in the past in order to produce nanocomposites with well-dispersed structure, since the macromolecular chains of the polymer can be effectively incorporated between the nanoparticles and/or sheets of the nanoparticles with this method, i.e., the nanoparticles are likely to become a part of the polymer at a molecular level. The general principle of this technique involves the mixing of nanoparticles with monomer (or multiple monomers) or a solution of monomer, followed by in situ polymerization in the presence of the dispersed nanoparticles. However, this method demands a low viscosity; the high viscosity of even dilute dispersion of graphene makes bulkphase polymerization difficult. During polymerization, if functional groups on the chemically modified graphene are reactive with the monomer, grafting of polymer macromolecular chains onto graphene surfaces can occur. This will not allow the graphene to form an interconnecting network, which ultimately leads to lower electrical conductivity values, but may be advantageous for mechanical reinforcement, resulting in better stress transfer from the matrix to the filler and improved barrier properties.

Solution (or solvent) mixing is a technique based on a solvent system in which the polymer or pre-polymer is solubilized and graphene are allowed to swell. In this method,

polymer or pre-polymer is dissolved either with the graphene in the same solvent or it is already in solution and is mixed with graphene by high-speed shear mixing, ultra-sonication or stirring, etc. Commonly used solvents include water, acetone, chloroform, tetrahydrofuran (THF), dimethyl formamide (DMF), toluene, and Methyl-2-pyrrolidone (NMP); some have been developed into commercial products. Graphene or functionalized graphene can be dispersed well in a suitable solvent owing to the weak forces that stack the layers together. The polymer then absorbs onto the delaminated sheets and when the solvent is evaporated the sheets reassemble, sandwiching the polymer to form the nanocomposites. This method may not be able to reach molecular level of dispersion as in situ polymerization.

These two above mentioned methods are applied to both thermosetting and thermoplastic polymers to synthesize GMPs (and other nanoparticles modified polymers). Typical thermoplastics based GMPs that have been processed by these two methods include: polystyrene (PS), poly(methyl methacrylate) (PMMA), thermoplastic polyimide (PI), poly(vinyl alcohol) (PVA), poly(ethylene terephthalate) (PET), some elastomers polyethylene-graphene maleic anhydride (PE-g-MA), polypropylene (PP), poly(vinyl chloride) (PVA), ethylene vinyl acetate (EVA)^{4, 5}. In spite of the high dispersion efficiency, these two methods cannot reach high-enough content of nanoparticles which sometimes is needed for multifunctionalities. Quite often liquid media (e.g. solvent) is involved in these two processing methods, traditional dispersion techniques are sonication (tip and bath), high-speed mechanical stirring and shearing mixer, which can produce good dispersion at low graphene loadings. Three-roll milling has been identified as a promising approach for dispersing higher fractions of nanoparticles (compared to the fractions achieved by sonication and stirring) in thermoset resins in large volumes; in this technique, high viscosity is favoured⁶.

Melt compounding is well known as the most economically attractive and scalable method for dispersing (nano)particles into polymers, particularly thermoplastics and is in most cases free of solvent. In this method, polymer is mixed mechanically with graphene or functionalized graphene then compounded at elevated temperatures (usually above the melting temperature of the thermoplastic polymer) via extrusion in most cases. The high shearing forces and pressure generated during melt compounding are the main force for intercalation or exfoliation. A wide range of thermoplastics (both polar and non-polar) based nanocomposites have been prepared using this method. It was the first time, to the best knowledge of the author that Herceg et al. reported using extrusion based on a powder based processing route to manufacture thermosetting nanocomposites with 20 wt % CNTs; the high shear mixing ensured good dispersion and distribution of CNTs in the thermosetting resin⁷. This could inspire the idea of processing GMPs based on thermosetting resins in a readily scalable way.

However, melt compounding has some inherent drawbacks that limit its application by not providing the same level of dispersion as solution mixing or in situ polymerization methods:

- The very low bulk density of graphene (approximately 0.004 g/cm³ based on a volumetric expansion) makes handling of the dry powder difficult and poses a processing challenge, such as feeding into processing equipment like an extruder. The spreading of the graphene particles in air can also cause high environmental and health risks
- The high viscosity of polymer melt along with the addition of graphene can significantly obstruct the effective dispersion of graphene
- The high temperature (for melting the thermoplastic) can cause the reduction of chemically modified graphene due to its thermal instability
- High shear forces that are usually applied in order to overcome the viscosity of the matrix for dispersion can lead to the breakage of the graphene sheets and scission of polymer chains.

Instead of using nanoparticle dry powder for melt compounding, two alternatives can be considered or has been developed for higher safety and/or compounding efficiency. One way is to use a **medium assisted melt compounding** technique, which represents a combination of solution-assisted and traditional melt mixing methods, and has been commercially applied for years. Clay modified thermoplastic nanocomposites have been processed using this technique⁸. So far there have not been accessible literatures reporting graphene nanocomposites processed by this method to the best knowledge of the author, which, however, can be reasonably envisaged. Water can be a suitable and environment friendly solvent. However, the graphene aqueous suspension will not possess good stability without the aid of dispersant or chemical modification on graphene. Recent research has indicated that nanocellulose can act as green and excellent aqueous dispersion agent for 1D (SWCNTs)⁹ and 2D (boron nitride (BN), molybdenum disulfide (MoS_2))¹⁰ energy materials. It is hence reasonable to speculate that nanocellulose can also be beneficial for the dispersion of graphene in water. On the other hand, practical information of a number of key aspects, such as the design of extruder (e.g. location of high-pressure pump and vacuum valve, screw element design, etc.) and control of water (or other solvents) amount, is still very short of for using this technique to process graphene/polymer nanocomposites. The other alternative is to use *masterbatch* that has high content of graphene. Thermoplastic based graphene masterbatch is usually in pellets form, therefore can be mechanically mixed with thermoplastic matrix (also in pellets in many cases) then melt compounded to reach different lower graphene contents. Development of masterbatch has been an important interest of customers and some commercial graphene producers. Graphene masterbatch products based on a number of general and engineering thermoplastics have been commercialized, including

HDPE, LDPE, LLDPE, PP, PS, PA, ABS, HPVA, EVA, PET, PLA, PC, PBT (suppliers can be found in the Appendix). Notably, commercial products of thermoset polymer based masterbatch are also appearing, such as the epoxy/graphene (20 wt %) masterbatch based on customized resin (NanoXplore, Canada, <u>http://www.nanoxplore.ca/products/</u>).

2.1.2 General discoveries of processing-structure-property interrelationship in GMPs

References 11 (cited 1713 times), 4 (cited 1556 times) and 12 (cited 1370 times) are the three most cited review articles for GMPs, i.e., graphene/polymer nanocomposites (via Scopus search tool), which reviewed the progress in this field until 2011 based on a large number of research work, thus can give a clear clue on quite a few technical aspects of high importance. The change of mechanical^{13, 14, 15, 16, 17, 18, 19, 20, 21}, electrical^{21, 22, 23, 24, 5, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34}, thermal^{35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52} and barrier^{25, 53, 54} properties of polymers depends significantly on the processing (mixing) method^{15-18, 25, 54, 55}, polymer structure, and morphology and surface functionalization of graphene, and can be correlated well with the change of crystallization behaviour^{56, 57, 58, 59, 60}, viscoelastic properties^{26, 28, 61, 62,} and relaxation performance^{63, 64, 65, 66, 67} of polymers. Specific research results that have been enumerated in these articles will not be repeated again in this review. General rules of the influence of morphology and dispersion/exfoliation of graphene as well as graphene-graphene and graphene-polymer interaction on properties of GMPs are summarized as below.

There are both rheological and electrical percolation thresholds; the latter is often slightly higher than the former, due to the requirement for closer proximity between platelets for particle tunnelling (approximately 5 nm) to reach electrical percolation.

The rheological percolation threshold determined from linear viscoelastic measurement can reflect dispersions of graphene (or other inclusion particles) in polymers and graphenepolymer interactions. For both percolation thresholds in common: randomly oriented, welldispersed graphene would be expected to percolate at lower concentrations than aligned, welldispersed platelets because the contacts between aligned particles would reduce at least at relatively low concentrations; a higher aspect ratio lead to a lower percolation threshold and higher electrical conductivity; wrinkled, folded, or otherwise non-ideal platelet conformations may raise the percolation threshold. It is thus understandable that thermal treatment, such as annealing, may benefit random orientation of graphene leading to lowered percolation threshold.

Relaxation characteristics, most directly, glass transition temperature, can also reflect the graphene-polymer interaction (covalent and non-covalent bonding, mechanical interlocking due to the roughness of nanoparticles) and additionally graphene dispersion: a strong polymer-matrix interface, which can induce good dispersion of particles, can restrict the chain mobility and thus tends to raise the T_g . A strong interface and high degree of dispersion may

not necessarily yield the lowest onset of electrical percolation, as a sheath of polymer may coat the surface of well-dispersed filler and prevent direct interparticle contact. Hence, decrease of T_g in combination with increased electrical percolation threshold has been noted.

The influence of graphene morphology and graphene/polymer interface on the mechanical properties can be concluded as:

1) compliant sheets or thin platelets commonly adopt a wavy or wrinkled structure, which may reduce the modulus as crumpled platelets would tend to unfold rather than stretch inplane under an applied tensile stress;

2) restacking, re-agglomeration or incomplete exfoliation could also lead to lower modulus values due to the decreased aspect ratios, on the contrary, good dispersion (sufficient exfoliation and uniform spatial distribution), strong interfacial adhesion and alignment of graphene will benefit the enhancement of mechanical properties.

For semicrystalline thermoplastics, formation of a crystalline layer around the platelets may also enhance stress transfer; the change of crystallinity and crystal form can also be an important factor correlated to the change of mechanical properties. Increased amount of γ -phase could be beneficial for the increase of toughness. However, care has to be taken when using crystalline performance to tailor properties since too high crystallinity will impair the ductility or toughness and electrical conductivity.

The geometry of graphene can impart significant anisotropy to the thermal conductivity of GMPs, with the measured in-plane thermal conductivity as much as ten times higher than the cross-plane conductivity. Similar to electrical conductivity, close interparticle contact also reduces thermal resistance thus increases thermal conductivity of the GMPs; good graphene/polymer interface can promote the thermal conductivity, however, too strong interface may have negative effect due to the formation of a polymer sheath on graphene. The negative coefficient of thermal expansion (CTE) of graphene can significantly lower the CTE of a polymer matrix. As has been reported, graphene can decrease the CTE of polymer more efficiently than CNTs. The thermal stability of polymer can be increased by graphene, which, however, is not always the case when GO is used since GO itself is not thermally stable. Both increased and decreased thermal stability of polymers with the addition of GO has been reported. Furthermore, it has been suggested that thermal stability of polymers can be improved with increased levels of exfoliation and interfacial adhesion.

The alignment of graphene (and other conductive particles) can also be realized under certain fields, typically an electrical field. The application of a strong electrical field along the thickness direction of membranes of graphene/poly(vinylidene fluoride) (PVDF) nanocomposite prepared by solution mixing and casting, led to the alignment of graphene perpendicular to the membrane surface. The maximum increment of thermal conductivity of the nanocomposite membrane was 212 % with respect to neat PVDF, which was further enhanced to 226 % when graphene was aligned with the electrical field⁶⁸.

The incorporation of graphene can significantly reduce gas permeation through a polymer, by providing a 'tortuous path' which inhibits molecular diffusion through the matrix. Orientation of the platelets may further enhance barrier properties perpendicular to their alignment. Higher platelet aspect ratios also facilitate increased barrier resistance.

2.1.3. Influence of melt compounding conditions on structures and properties of thermoplastic based GMPs

Since the majority of thermoplastic based nanocomposites are processed using melt compounding techniques, it is very important to understand the influence of compounding conditions in extruder and injection moulding which are the two most commonly used melt processing techniques, on the structures and properties of the resultant GMPs. An EU project, NanoMaster⁶⁹, studied systematically the influence of extrusion and injection conditions on the structure and properties of graphene reinforced thermoplastic composite materials.

It has been found that high shear forces generated in both extrusion and injection moulding were beneficial for enhanced mechanical properties but detrimental to electrical conductivity, due to the promoted disruption of the conductive network structure. Therefore, the shear conditions need to be adjusted by tuning parameters such as screw elements, processing (extrusion or injection) rate and temperature to reach required mechanical or electrical properties. Barrel temperature and injection speed have more significant effect on the electrical resistivity of the moulded compounds than mould temperature. Lowering the barrier temperature increases melt viscosity, resulting in higher injection pressure, which will generate higher shear forces and higher resistivity. Injection at high speed generates high shear forces, which is believed to contribute to lateral size reduction of graphene and thus increases resistivity.

A skin-core structure is commonly formed in injection moulded parts where the outer surface has a lower filler concentration than the inner part. In the skin layer there is also an increased orientation of particles relative to the inner layer, due to the fountain-like flow at the melt front which orients the polymer macromolecules and filler particles in the flow direction. At the cold mould wall the particles will immediately solidify and their orientation will be frozen, leading to higher electrical resistivity at the surface than in the bulk. Hence, thin-walled parts will need higher filling pressure and will show higher orientation in the flow direction due to higher shear forces generated at the mould surface. As a consequence, the electrical resistivity in thin sections will be higher than in thicker sections of a part, and thinner parts will show higher Young's modulus in flow direction. The skin effect can be reduced by optimizing temperature and injection speed. Electrical conductivity also varies along the flow path of the molten material. Higher melt pressure close to the gate results in stronger filler orientation in flow direction consequently high electrical resistivity, while

lower pressure farther away from the gate results in weaker particle orientation consequently lower resistivity.

Thermal conductivity of the GMPs increases with increasing graphene content, which, however, does not show strong percolation behaviour. The difference between in-plane and through-plane thermal conductivity, due to the geometry anisotropy of graphene, can be reduced by lowering the shearing.

2.1.4. Typical examples of thermoset based GMPs relative to processing methods and functionalization of graphene

Entanglement of CNTs in a matrix at sufficiently high loadings can result in undesirably large viscosity increases, whereas graphene platelets can more easily slide past one another moderating the viscosity increase^{70, 71}, hence from a processing point of view thermoset resin modified by graphene may be more favoured than by CNT for advanced FRP composites. Functionalization to enhance compatibility of graphene with the monomer or precursor of resins may help to further moderate the solution viscosity. External field, typically electrical field, can also be used to orientate or align graphene in thermosetting polymers during the curing process⁷².

Lee et al. ⁷³ prepared thermally exfoliated GO using a method developed by a Princeton University research group^{74, 75}. The resultant functionalized graphene single sheet contained C-OH and -COOH groups. Such functionalized graphene was used to modify epoxy, leading to improved strength and toughness by about 30-80 % and 200-700 % at room and low temperatures of -130°C, respectively, reduced CTE at both below and above T_g by about 25 % at loading of 1.6 wt % functionalized graphene, and increased T_g by about 8°C at 0.4 wt % FGSS, without deteriorating the processability. The modified epoxy resin is promising for the use in next generation multifunctional cryotank CFRP composite applications.

Graphene, when partially exfoliated in epoxy, was already able to change the decomposition pathway of epoxy at high temperature, enhance the thermal stability and promote the formation of char residue, hence decreased the melt flow and inhibited effectively the flammable drips of epoxy during combustion (at 0.5 wt% GNS)⁷⁶.

Different chemically modified graphene, such as GO⁷⁷, ethyl isocyanate-treated GO (iGO)⁷⁸, octadecylamine (ODA)-functionalized GO⁷⁹, 3-aminopropyltriethoxysilane (APTSi)-functionalized GO⁸⁰, amino-functionalized GO⁸¹, and rGO⁸², were incorporated into thermosetting polyimide (PI) resin, using in situ polymerization and solution mixing technique, respectively. Enhanced mechanical and electrical properties, moisture barrier property, thermal and tribological properties as well as hydrophobic properties were reported. With 0.38 wt % of iGO (mixed by in situ polymerization), the Young's modulus and tensile strength of PI was increased by 30 % and 8 %, respectively, and the electrical conductivity was increased by more than eight orders of magnitude. ODA-functionalized GO led to a

larger improvement of Young's modulus (by ~96 %) and tensile strength (~41 %) compared to GO; APTSi-functionalized GO led to even larger improvements in Young's modulus (by 132 %) and tensile strength (by 79%) of PI at 1.5 wt % particles, along with enhancement of electrical and thermal conductivities which were ~10¹⁰ and two times higher than those of pure PI, respectively. 0.001 wt % well-dispersed GO (by solution mixing) led to 83 % reduction in the moisture permeability rate, 95 % improvement of transmittance in the visible light range and much lower CTE (41 ppm °C⁻¹ compared with 59 ppm °C⁻¹ for neat PI). Such nanocomposites are potential candidates for the applications such as the substrates of advanced touch panel or flexible display, where high optical transparency and good water resistance are essentially required. XRD analysis showed that GO was fully exfoliated in PI resin. The modified PI resin also showed much lower friction coefficient and higher abrasion resistance, thus can be a potential candidate for tribological-materials.

2.1.5. FRP composite based on graphene modified thermoplastic polymers

Open access literature reporting the use of graphene modified thermoplastic as matrix for fibre reinforced composites are hardly found, particularly when continuous fibres or fibre fabrics are used. The difficulty of impregnation due to high viscosity of thermoplastics melt and fast solidification below the melting point may be one main reason. Impregnation of fibres or fibre fabrics in combination with in situ polymerization or solution mixing of graphene modified thermoplastics may be promising options. Larkin et al. reported spray coating graphene onto the surface of plasma treated poly-ether-ether-ketone (PEEK)/CF ply and preparation of graphene modified PEEK/CF laminates by pressing 20 such plies at elevated temperature⁸³. This work was, however, not strictly based on graphene modified PEEK. On the other hand, there have been commercial products of long GFs and CFs reinforced thermoplastics, such as the products from SGL group where CFs and GFs are bonded with PA6 with the aid of special sizing in the form of long fibre-reinforced pellets, UD tape and sheets, and woven. Collaboration with these companies may facilitate the production of GMFRP composites based on thermoplastics. Furthermore, it is still possible to impregnate fibre reinforcement using thermoplastic based GMP melt given high temperature and pressure are used to facilitate the flow of melt and the fibres are not densely packed.

On the other hand, it can be relatively easier to process thermoplastics based GMFRP composites using short fibres. An Interreg Nord project, Smart WPC (2017-2019) (https://www.swerea.se/publikationer/swerea-sicomp-e-news, www.centria.fi/smartwpc) aims to develop advanced wood plastic composites (WPCs) based on graphene modified thermoplastics in order to extend the use of WPCs in more versatile applications. The results of this project are expected to fill the knowledge and technology gaps and promote functionalized bio-based composites for innovative products.

2.1.6. FRP composite based on graphene modified thermoset polymers

The use of graphene or functionalized graphene modified thermosetting resins, mostly epoxy, in FRP composites has been initiated^{84, 85}. The results also implied great potential of the modified resin for prepreg technology.

Graphene was mixed into epoxy resin together with two flame retardants, Melamine phosphate (MP) and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) under higher shear (1000 rpm) for 30 min at 25°C prior to the addition of hardener⁸⁴. The glass fibre reinforced polymer (GFRP) composites using such modified epoxy was prepared using a hand lay-up method followed by vacuum bagging. The graphene was well dispersed within the matrix, showing multi-layered intercalated and exfoliated structure, which, tended to re-stack forming some agglomerates during composites processing and curing. The fractured surfaces showed that protruding graphene fillers were thickly coated with absorbed polymer, suggesting strong polymer-graphene interactions. The addition of the flame retardants decreased the mechanical properties of epoxy in spite of increased flame retardancy. The presence of graphene helped in restoring mechanical properties close to neat resin and further improved the flame retardancy due to its good barrier effect.

One study also reported the enhanced intercalation of epoxy monomer between expandable graphite (EG) layers by using an epoxy resin containing surface-active agents leading to 'stacked' graphene or few graphene layers in epoxy. Such modified epoxy based CFRP and Kevlar reinforced composite showed significantly improved thermal stability at elevated temperatures and a reduction of surface electrical resistivity⁸⁶.

Thermally reduced graphene oxide (TrGO, 0.3 wt % and 0.5 wt %, respectively) was dispersed in epoxy using a three-roll mill which has been proven to be more efficient than other methods such as vacuum stirring or ultrasound dispersion⁸⁷. CFRP and GFRP prepregs based on such modified epoxy were manufactured using a filament winding technology, followed by the manufacture of laminates in an autoclave. In spite of decreased strength due to formation of voids because the viscosity of epoxy was increased with the addition of graphene hence enclosed air cannot be removed, the residual compressive properties (from a compression after impact (CAI) test) of the so-processed laminates was improved significantly - the GFRP showed the highest improvement of 55 % with 0.3 wt % TrG-O in the resin.

TEGO was introduced into epoxy based CFRP composites through 3 methods: electrosprayed on the CF surface, dispersed into the epoxy resin, and combination of the previous two methods, respectively⁸⁸. It was found that all modified composites gained multifunctionalities - improved stability at elevated temperatures, electrical conductivity, thermal diffusivity and self-heating capability, which enable such composites very promising as de-icing structural parts that can be widely used for aerospace, aeronautics, energy and automobile industries. Furthermore, the significance of the modification efficiency followed the order: graphene simultaneously in matrix and on CF>graphene in matrix>graphene on CF.

Masterbatch based on different thermosetting resins is also of high interest for more cost effective production. However, the availability of masterbatches relies heavily on the capability of the graphene-product producers to develop customized graphene and process the masterbatch with uniform dispersion and sufficient intercalation/exfoliation.

In 2016, several Vinnova projects were funded, including one to develop graphene modified epoxy resin with improved mechanical properties and radar signal transmission as well as tailored dielectric properties in GFRP composites used for aircraft radome application⁸⁹, and one to develop graphene modified CFRP for long term high temperature applications that may be potential for high-temperature parts in aircraft engines, as well as to develop graphene modified thermosetting resins with improved mechanical and barrier properties for general application in aircraft parts⁹⁰.

2.2. Composites based on graphene coated fibre reinforcement

In spite of efficient enhancement of properties, reduced flowability of polymer matrix with the integration of nanoparticles can still restrict the processing of FRP composites. Higher temperature and pressure during processing are usually needed which pose more critical demand on the equipment. Furthermore, the graphene nanoparticles may have the risk to be filtered out by the micro-scale fibres leading to an uneven distribution that impairs the homogeneity and overall properties of the resultant composites. In addition, residual solvents, if not removed thoroughly, can also have a negative influence on the final properties of the composites. As an alternative, graphene nanoparticles can also be doped onto the surface of fibre reinforcement, resulting in a 3D effect between plies under loading. Notably, this method will generate the most pronounced effect on the fibre-matrix interface, modifying interlaminae fracture toughness, hardness, delamination resistance, etc. Graphene doped fibres used for strain monitoring, pressure sensing, fluid flow monitoring application were reported. Different coating means have been used, including soaking, dip coating, electrospraying and electrophoretic deposition. The coated continuous fibres or fibre fabrics/woven can be used as they are, and can also be chopped down to short fibres used in the process, such as sheet moulding compound (SMC) or melt compounding.

GO can be dispersed in fibre sizing agents and then coated on the surface of fibres by pulling the fibres through or dip the fibres into the modified sizing agent. The interfacial shear strength (IFSS, evaluating the microbond of single fibre to matrix) of the epoxy composites with the coated CFs was improved by maximum 70.9 % and the interlaminar shear strength (ILSS, evaluating the interlaminar bonding of composites) was improved 12.7 % compared with the composite with desized CF and the commercially-sized CF, respectively⁹¹. Additionally, the tensile strength and modulus of GO coated CF reinforced epoxy composites were also higher than those of the normal composites. The microscopic study (Figure 2)

indicated that the commercial-sized CF composites failed predominantly by progressive interfacial debonding and fibre pullout followed by breakage of fibres. The pulled-out fibres had a clean surface, indicating a weak interfacial bonding between the matrix and fibre. In contrast, GO coated CF composites revealed the simultaneous breakage of fibres and matrix, the interfaces between the fibre and the matrix were almost intact even after failure, which evidenced strong interfacial bonding.

Electrical conductivity and strain monitoring capability of composites reinforced by GFs dip-coated by non-functionalized graphene and amino functionalized graphene, respectively, were evaluated⁹². The electrical conductivity of the composites with coated GF fabrics were $(9\pm7)\times10^{-5}$ and $(5\pm1)\times10^{-2}$ S/m corresponding to non- and amino-functionalized graphene coating, respectively, higher than the values using MWCNTs⁹³. The electrical network conferred sensorial properties to the GF fabric. At strain values below 0.015 mm/min the normalized electrical resistance grew exponentially. When GF breakage visually occurred, the normalized electrical resistance increased abruptly because of the progressive loss of contact between graphene nanoparticles until the connectivity of the electrical network was lost. These findings are very interesting for smart textiles applications.



Figure 2: SEM images of fractured surfaces of unidirectional CF composites: (A) commercial-sized CF-reinforced epoxy composite, (B) 5 wt% G-O sized CF-reinforced epoxy composites, (C) 10 wt % G-O sized CF-reinforced epoxy composite (Reprinted with permission from Ref. [91], Copyright 2012, American Chemical Society)

The applicability of graphene-coated piezo-resistive fabric for liquid composite moulding (LCM) processing monitoring was explored by Ali et al⁹⁴. Sheets of glass fabrics were soaked in GO aqueous suspension overnight and dried, followed by a chemical reduction process

using HI acid to obtain rGO coated GF. The rGO coated fabrics exhibited an electrical resistance that changed under applied loading and during mould filling. The discovery proposed a novel solution to use graphene coated peel ply as a sensor.

Short carbon fibres (SCFs) were added into a GO aqueous suspension under stirring for 24 hours, followed by drying to remove water. SCF/polyethersulfone (PES) composites, with uncoated and GO-coated SCFs, were prepared by extrusion and injection moulding⁹⁵. It was found that the gaps between the pulled-out fibres and the PES matrix became much smaller and even disappeared at 77K (liquid nitrogen temperature) and the amount of PES attached onto the pulled-out SCF surfaces was much more at 77K than at room temperature. The tensile strength and Young's modulus of the composites at 77K was improved by ~17 % and ~41 %, respectively, with 12.5 wt % GO-coated SCFs; the flexural strength and modulus was improved by ~29 % and ~39 %, respectively. Furthermore, these cryogenic mechanical properties of the composites with GO-coated SCFs were higher than those of the composites via separate addition of GO and SCFs in PES.

Electrophoretic deposition (EPD) is an attractive technique for manipulation and deposition of graphene on different substrates⁹⁶. EPD in its simplest form requires the application of an electrical potential to electrodes immersed in nanoparticle dispersion. Two sub-processes take place during EPD⁹⁷:

(1) electrophoretic movement of suspended charged particles in a liquid phase towards an electrode under the effect of an electric field;

(2) collection of the particles at the electrode surface and formation of a deposit.

The key precondition for successful EPD of particulate materials is the formation of a stable suspension of charged particle. The stability of the suspension, its concentration, and the size of the suspended species affect the quality (uniformity, density and roughness) of the resulting deposits. Both aqueous and non-aqueous suspensions have been used for the EPD of graphene, while the most common strategy is the use of GO as the starting material in the suspension. Surfactants (charging additives) are used in many cases to provide high zeta potential and electrophoretic mobility to the suspended particles as well as keep the suspension stable.

GO and rGO (noted that the rGO deposits were formed by depositing GO onto fibre reinforcement followed by reducing the GO deposits) have been used to coat CF and GF - continuous fibres, fabrics/woven and chopped fibres, using EPD method. The treated fibres have been used in composites based on both thermoplastics and thermosets^{98, 99, 100, 101, 102, 103, 104, 105, 106}. Surface wettability of CFs by epoxy resin was significantly improved due to increased surface free energy of the fibres by the deposition of GO; a significant improvement of both IFSS (56 %-70%) and ILSS (55 %) confirmed the remarkable improvement in the interfacial adhesion of the composites^{98, 99, 102, 103}. The rGO deposited CF was found to be more effective than CF to improve the EMI shielding property

of the composites – the shielding effectiveness of the composites with rGO deposited CF was 16.3 % higher than that of CF/PU composite¹⁰⁰ and 47.6 % higher than that of CF/epoxy composite¹⁰¹. Fragmentation tests showed significantly higher IFSS (GF/epoxy) value for GO deposited GF over bare GF with increment up to a factor of about 2 (219 %) and proportional to the amount of GO deposit; nanoscale delamination test showed a failure of the composite at the GO/epoxy rather than at the GO/GF interface¹⁰⁴. PVC based WPC with CF, GO-deposited CF (via EPD) and rGO-deposited (by reducing GO deposits on CFs) CF were prepared by melt compounding¹⁰⁷. 4 wt % CF was found beneficial for the improvement of EMI shielding effect of WPC; deposit of rGO on CFs further improved the EMI shielding effect by 26% relative to the WPC with 4 wt % plain CF.

Swerea SICOMP AB, Sweden, has been leading the innovation work of doping CNTs on fibre reinforcement, using EPD method for the production of polymer composite/metal hybrid joints (EU FP7 project, SAFEJOINT) and high performance multifunctional CF based composite structures (EU H2020 project, MODCOMP). Particularly in the MODCOMP project, a prototype EPD setup was developed, which can perform the deposition onto fibres and fabrics/woven in a continuous way, hence highly increases the production efficiency (against the most previous and ongoing studies that worked with non-continuous EPD) and significantly reduces the use of nanoparticle suspensions and their waste¹⁰⁸. This EPD prototype can scale up the production of CNTs and graphene deposited fibre reinforcement reaching TRL 5-6, which is currently under an internal patent review process.

2.3. Composites made of graphene modified prepreg

As previously described, graphene modified polymer matrix is very promising for prepreg technology in lightweight, high-performance and multifunctional FRP composites.

Tetrahydrofuran (THF), a special organic solvent that can be easily removed by a rotary evaporation under vacuum, was selected owing to its superior properties over other traditional organic solvents, to prepare homogeneous GO dispersion for epoxy resin. The mixture of epoxy and GO (after expelling the solvent) was dissolved in acetone with the curing agent followed by sonication to prepare modified epoxy with various GO contents. Afterwards, the GO modified epoxy was brushed onto plies of CF fabrics with a defined unit weight to prepare GO modified CF/epoxy prepregs¹⁰⁹. It is noted that after being held at room temperature for 3 hours the GO/epoxy dispersion containing curing agent remained uniform; while after 12 hours, precipitation of agglomerated GO nanosheets occurred. The time for keeping stable (3 hours) was regarded sufficient to complete the prepreg processing at labscale. An enhancement of ILSS by 8.05 % was reached at the GO content in epoxy resin of 0.10 wt %.

The GO modified epoxy resin was also prepared with the aid of ethanol for the GO dispersion prior to mixing with epoxy. The CF prepregs was prepared by impregnating the CF

fabrics with the epoxy/GO mixture. 0.3 wt % GO in the CF/epoxy composites led to flexural strength increased by 66 %, flexural modulus by 72 % and ILSS by 25 %. The enhancement in the properties of the composite was due to the improvement in properties of epoxy resin and interfacial interaction between CF reinforcement and matrix by hydrogen bonding as well as mechanical interlocking of GO with CFs and epoxy resin¹¹⁰.

The effect of GO and partially thermally reduced GO (RRGO, by treating the GO in N₂ for 4 hours at 150°C, 200°C and 250°C, respectively) on the thermal stability and mechanical properties of CF/bis-benzoxazine (B-BOZ) composites processed using prepreg based on GO or PRGO modified B-BOZ was studied¹¹¹. THF was also used for the preparation of GO or PRGO dispersion which was mixed with B-BOZ. The prepreg was made by a melt impregnation method by which unmofidied or modified resin was brushed over CF fabrics on a steel plain at 90°C, respectively. The addition of GO decreased the thermal stability, flexural properties and ILSS of B-BOZ. In contrast, by virtue of excellent thermal resistance, graphitization acceleration, and the folds deformation of PRGO, not only the thermal stability of B-BOZ was improved, but also the mechanical properties. With 0.25 wt % and 0.50 wt % of PRGO in the B-BOZ resin, the maximum improvement of flexural strength, flexural modulus and ILSS can be 22 %/16 %, ~9 %, and 29 %/23 %, respectively (note that lower content of PRG-O resulted in higher properties improvement, however, the maximum properties did not occur always at the same PRGO).

Zyvex Technologies (Ohio, USA) has developed Arovex[®], a commercialized prepreg product reinforced with CNTs and graphene (<u>http://www.zyvextech.com/arovex/</u>) based on their molecular chemicals called Kentera, which allows nanomaterials to be evenly dispersed in to a resin system. Compared to industry leading CF prepreg, Arovex[®] CF prepreg shows higher flexural modulus, tensile strength, compressive modulus, fracture toughness and ILSS by 35 %, 26 %, 12 %, 194 % and 20 %, respectively.

The graphene or functionalized graphene coated fibres can also be expected for prepreg preparation, although there has been few accessible publication.

2.4. Application of graphene buckypaper

Similar to CNT buckypaper, graphene and GO can also be assembled into paper-like materials. The graphene or GO paper is a self-supporting thin film that consists of aligned graphene or GO nanosheets¹¹². The well-ordered GO paper exhibits outstanding mechanical properties such as up to 40 GPa Young's modulus and up to 125 MPa tensile strength which surpass many other paper-like materials like graphite foil. The individual graphene oxide nanosheets with their interlocking-tile microstructure are the reason GO paper has high strength and modulus¹¹³. Intercalation of polymer layers and chemical cross-linked between the GO sheets can be used for improving the mechanical properties of GO paper.

To produce graphene and GO papers, different methods have been used such as: vacuum filtration assembly, evaporation induced self-assembly, spin coating, drop casting, Langmuir-Blodgett (L-B), spraying, dip coating and Langmuir-Schaefer¹¹³. Free standing GO paper materials show remarkable mechanical stiffness and excellent flexibility combined with outstanding electrical properties, hence, are potentially suitable for flexible electrochemical active materials such as electrical batteries, fuel cells, biomedical devices and supercapacitors. Liang et al. reported synthesis of PVA/GO composite paper via a water solution processing method¹¹⁴. The resulting composite paper has increased tensile strength and Young's modulus by up to 76 % and 62 %, respectively, with the addition of 0.7 wt % GO. Graphene papers, which usually exhibited a shiny metallic luster on both sides, exhibit room-temperature electrical conductivity of 7200 S/m and remarkable tensile strength up to 35 GPa, which enable graphene paper to be a freestanding electrode. Shah et al. developed conducting polythiophene/graphene nanocomposites, which were electrically conductive with a low graphene concentration¹¹⁵. Outstanding water resistance and high thermal stability are excellent properties of graphene paper compared with GO paper. The mechanical properties (e.g. tensile strength and strain) of graphene composite paper are usually higher than those of graphene paper due to improved mechanical interconnection among the polymer/graphene layers. The higher tensile strength determines the mechanical durability of polymer/graphene composite paper for flexible supercapacitors as binderless and current collector-free electrodes¹¹³.

So far the reported study on the application of graphene buckypaper in FRP composites mainly focused on the function as outer protection layers. Subsequent to the work of developing novel flame retardant CFRP composites using CNT buckypaper^{116, 117, 118}. Wu et al. fabricated CNTs/graphene hybrid membranes which were applied on the surface of CFRP composite plates as flame retarding layers (Figure 3)¹¹⁹. The membranes were prepared by vacuum filtering the aqueous suspensions of well dispersed nanoparticles followed by the steps of being thoroughly washed with deionized water and acetone to remove the surfactant, peeled off from filter and dried in a vacuum oven. The CF/epoxy composites with and without the membranes skin were fabricated by using hand layup processing followed by vacuum bagging, curing and post curing. The membranes skins were placed on both sides of a controlled CFRP composite (i.e., reference composite without membranes) plate: one piece of membrane on the top, and two pieces on the bottom of the CF laminate on a mold. Results showed that the incorporation of hierarchical MWCNT/graphene membrane with 7.5 wt % of graphene displayed a 35 % reduction in the peak heat release rate (PHRR) for the CF/epoxy composite plate, while the incorporation of MWCNT membrane led to just 11 % reduction in PHRR. A synergistic flame retarding mechanism is suggested to be attributed to the results, which includes controlling the pore size and penetrative network structure.



Figure 3: A photograph and SEM images of MWCNT and MWCNT/graphene nanoplatelet membranes (Reprinted with permission from Ref. [119] Copyright © 2013 Dongxian Zhuo et al.

3. Multi-scale modelling of graphene modified polymeric composites

Modelling and simulation allow methodical variation of material properties beyond the capacity of experimental methods. The focus of this chapter is not on listing various equations but expounding the mechanisms or reasons behind or for the modelling.

3.1. Modelling and simulation of GMPs

Atif and Inam published¹²⁰ an article in 2016 reviewing thoroughly the progress in the last decade in the modelling and simulation of GMPs in terms of graphene structure^{121, 122}, topographical features^{123, 124, 125}, interfacial interactions^{126, 127}, dispersion state^{128, 129}, aspect ratio¹³⁰, weight fraction^{130, 131}, and trade-off between variables and performance, such as mechanical properties, thermal and electrical properties.

Dai and Mishnaevsky developed a 3D computational model of graphene reinforced polymer nanocomposites, by employing a special Python based software code and adapting it to the typical structures of graphene based composites, and applied the model for the analysis of damage and fracture mechanisms in the composites¹³². The graphene/polymer interface properties were determined using the inverse modelling approach. The effect of aspect ratio, shape, clustering, orientation and volume fraction of graphene on the mechanical behaviour and damage mechanisms of nanocomposites were studied in computational experiments. It was shown that Young's modulus of the nanocomposite increased with increasing aspect ratio, volume content, elastic properties of interface layer, and decreasing degree of intercalation. The tensile strength followed similar tendencies, except for the aspect ratio and clustering degree. Nanocomposites with homogeneous structures demonstrated much lower Young's modulus and strength as compared with aligned, plane graphene sheet reinforcement. The structural imperfections of graphene reinforcement (like crumpling shape or random misalignment) had considerable effect on the composite performance.

Pandele et al. used molecular mechanics and dynamic simulations at atomistic scale to investigate the mechanical behavior of graphene based chitosan composite with different graphene content¹³³. The energetically stable computational system presented a uniform and random distribution of polymer chains and graphene sheets. The improvement of Young's moduli depended on dispersion mode and interface interaction between graphene and chitosan. The elastic moduli of the composite increased with increasing graphene amount in the compotational bulk systems.

Manta et al. developed a simulation tool on the graphene/polymer nanocomposites electrical response based on the finite element method (FEM) built on the multi-scale multiphysics format consisting of a unit cell and an RVE¹³⁴. It was proven that the increase of the aspect ratio reduced the percolation threshold and increased the electrical conductivity of the nanocomposite for a given value of volume fraction. The percolation threshold of two material structures of the same constituents (PVDF/graphene) prepared with different methods was predicted, highlighting the effect of the materials preparation on the filler distribution, percolation probability and percolation threshold. The assumption of the random filler distribution was proven to be efficient on modelling material structures obtained by solution methods, while the through-the-thickness normal particle distribution was more appropriate for nanocomposites constructed by film hot pressing. One of the most important findings of this study was the capability to create constitution curves by plotting the effect of each examined parameter on the variables of the percolation law. These graphs could be used as preliminary design tool for more effective material system manufacturing.

3.2. Modelling and simulation of graphene modified FRP composites

Currently there is lack of research on the simulation of multi-scale composites including nanoparticle, microfibre and polymer matrixes.

Zhang simulated Young's modulus of graphene modified FRP composites by applying a two-step simulation shown in Figure 4. Halpin-Tsai equations were utilized to obtain Young's

modulus of graphene/polymer nanocomposites. The properties of the nanocomposites were employed to calculate the multi-scale composites using the woven-fibre micromechanics theory. The micromechanical model MESOTEX was chosen to simulate multi-scale composites, because it is a useful model for predicting the elastic properties of composites with a variable laminate geometry associated with classic thin-laminate theory. The modelling data showed a consistently higher improvement than the experimental data due to the agglomeration of graphene¹³⁵.



Figure 4: Schematic of two-step simulation of mechanical properties of graphene modified *FRP* composite

In the EU H2020 project, MODCOMP, a proper combination of analytical and computational material modelling techniques within a multi-scale framework is aimed to be developed for the purpose of analysing the effect of CNTs, CNFs and graphene on the target properties and functionalities of CFRP composites. The modelling work contains processing modelling with the attempt to develop numerical models to be used in offline process design, and multi-scale physical modelling with the attempt to analyse/predict mechanical, thermal and electrical properties of the nanomodified CFRP composites covering molecular dynamics simulation, mechanical/electrical/thermal response at nano/micro level and at yarn/fabric level, and modelling at macro-level (demonstrators).

Elmarakbi and Azoti reported a multiscale modelling of graphene modified polymer composite for automotive lightweighting or crashworthiness purposes³. A starting point of such modelling was the derivation of graphene sheets mechanical properties. The constitutive law of each phase in the composite was accounted for by a comprehension derivation of the mechanical properties. At the atomistic scale, the graphene sheet was considered undergoing non-linear deformations. A Taylor series expansion in powers of strain therefore established

the expression of its second order linear elastic modulus and third order non-linear elastic modulus. This enabled the derivation of a non-linear constitutive behaviour and thus based on the modified Morse potential. For the polymer matrix, a rate-dependent elasto-plastic behaviour was selected to account for the crashworthiness. It was also assumed that the matrix underwent ductile damage behaviour with either isotropic or kinematic hardening. The homogenized properties of the graphene modified polymer composites were derived by combining atomistic continuum approaches with micromechanics methods. An RVE was selected such as a graphene sheet embedded in the polymer matrix phase. To solve the heterogeneous material problem, the kinematic integral equation of Dederichs and Zeller was used for micromechanics problem leading to the derivation of the global concentration tensors of graphene and polymer phases. At this level, the multi-site version of the global concentration and distribution of the phases) and morphological (aspect ratio, volume fraction, mechanical properties) textures. Mean-fields approaches could therefore be applied for the overall response of the composite.

4. Conclusions

Integration of graphene into FRP composites is a very promising way to achieve advanced composites with lighter weight, higher performance and more functionalities relative to traditional FRP composites. The methods of integration that are used and can be considered for further development are reviewed in this study, which can include:

- Using graphene modified polymers as advanced matrix for the bulk composites or coating layers
- Doping graphene onto fibre reinforcement as interface modifier
- Using the combination of the two methods above
- Using graphene modified prepreg produced via the above three methods
- Using graphene buckypaper

The processing-structure-property interrelationship in graphene modified FRP composites along with the functionalization of graphene is also reviewed. Despite of inconsistency of reported results from different researchers, some general conclusions were reached:

- The most prominent influencing factors for the properties of modified composites include the aspect ratio of graphene nanoplatelets and surface functionalization; the dispersion and alignment of graphene; and the interactions of graphene-polymer and graphene-fibre reinforcement.
- The selection of processing techniques and tailoring of influencing factors depend on the desired properties. For instance, doped graphene onto fibre reinforcement can be more efficient than dispersed graphene into polymer to improve the interfacial and

interlaminar properties; well-dispersed and randomly oriented graphene can be more beneficial than well-dispersed and aligned graphene for higher electrical conductivity while less favored for higher mechanical properties; graphene buckypaper can be efficient for surface protection or functionalization.

- Higher shearing force and pressure beneficial for orientation of graphene and strong interaction between graphene and polymer can lead to enhanced mechanical properties, which can, however, increase the electrical conductivity threshold
- Higher aspect ratio of graphene nanoplatelets at least at low graphene contents is beneficial for lower percolation threshold and higher conductivity, modulus and barrier resistance. The effect of aspect ratio will fade with increasing graphene loadings especially when agglomeration appear
- Masterbatches with much higher graphene loadings can be a promising solution for scaling up the production of GMFRP composites, more cost effective and energy efficient.

The work performed now regarding GMFRP composites are generally at a low Technology Readiness Level (TRL). There are still big gaps of knowledge and technology that have to be filled before laboratory achievements can be applied into a pilot plant – or industrial scale production (high TRL). Industrial demand is a very important driving force behind the development of related knowledge and technology.

5. Acknowledgement

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6. Appendix: Review of graphene-based materials

6.1. Preparation, structure, grades and characteristic properties of graphene

As Nicholas A. Kotov¹³⁶ wrote in his review in Nature "When carbon fibers just won't do, but nanotubes are too expensive, where can a cost-conscious materials scientist go to find a practical conductive composite? The answer could lie with graphene sheets". Graphene is considered a **two-dimensional** carbon nanofiller with a **one-atom-thick planar sheet** of sp^2 **bonded carbon atoms** that are densely packed in a **honeycomb crystal lattice**. The carbon-carbon bond (sp^2) length in graphene is approximately 0.142 nm^{137, 138, 139}. Various groups

reported different thickness measurements for graphene layers, with thickness ranging from 0.35 to 1 nm, relative to the SiO₂ substrate¹⁴⁰. Novoselov et al. prepared graphene films and the apparent thickness given by atomic force microscope (AFM) for few-layer graphene, which could contain only 1, 2 or maximum 3 layers of graphene, was reported between 1 and 1.6 nm¹⁴¹. Graphene is regarded as the "thinnest material in the universe"^{142, 143}. ISO/TS 80004-13:2017 has clearly defined that the number of layers when a 2D materials becomes a bulk material varies depending on both the material being measured and its properties. In the case of graphene layers, it is a 2D material up to 10 layers thick for electrical measurement, beyond which the electrical properties of the material are not distinct from those for the bulk (also known as graphite)¹⁴⁴.

Graphene can be prepared using different methods^{145, 11, 146}, the most commonly used are:

- Chemical vapor deposition (CVD) on a metallic substrate (generally copper)
- Separation/exfoliation of graphite or graphite derivatives
- Epitaxial growth on electrically insulating surfaces such as Silicon Carbide (SiC)
- Reduction of graphene oxide.

One of the most attractive applications of nanoparticles is in polymeric composites due mainly to two reasons: 1) nanoparticles can overcome certain deficiencies and substantially enhance mechanical properties at low loadings, which ultimately result in low component weight; and 2) nanoparticles can enhance the multifunctional properties hence may create new applications of the bulk composites. For the purpose of producing advanced polymeric composites, graphene may be preferred over other nanomaterials, such as sodium montmorillonite (Na-MMT), layered double hydroxide (LDH), carbon nanotubes (CNT), carbon nanofibers (CNF), expanded graphite (EG), etc., owing to its high surface area, aspect ratio, mechanical performance, thermal conductivity and electrical conductivity, electromagnetic interference (EMI) shielding ability, flexibility, transparency, and low coefficient of thermal expansion (CTE)⁴. Table 1 gives a comparative chart on the mechanical, thermal and electrical properties of graphene with CNT, steel and Kevlar fibre.

Materials	Tensile strength	Thermal conductivity (W/mk) at room temperature	Electrical conductivity (S/m)
Graphene	130±10 GPa	(4.84 ± 0.44) x10 ³ to (5.30±0.48)x10 ³	7200
CNT	60-150 GPa	3500	3000-4000
Nanosized steel	1769 MPa	5-6	1.35×10^{6}
Kevlar fibre	3620 MPa	0.04	Insulator

Table 1: Representative properties of graphene, CNT, nanosized steel and polymers

6.2. Modification of graphene

Pristine graphene, however, is unsuitable for interaction with polymer chains, because graphene itself is hydrophobic, hence has a pronounced tendency to agglomerate in a polymer matrix^{147, 148}. Modification of graphene using chemical, electrochemical or other methods (such as π - π interaction¹⁴⁹), is usually needed. The functional groups attached to graphene can be small molecules^{150, 151, 152} or polymer chains^{149, 153, 154, 155}.

Chemical modification of graphene is based on the modified Hummers (and Offeman) method¹⁵⁶, using strong oxidizing agents, more specifically a mixture of potassium permanganate (KMnO₄) and sulphuric acid (H₂SO₄) and sodium nitrate, to initially prepare graphite oxides (C:O ratios of approximately 2:1) followed by an exfoliation, reduction or functionalization process. Oxidation disrupts the delocalized electronic structure of graphite and imparts a variety of oxygen-based chemical functionalities to the surface¹⁵⁷: hydroxyl and epoxy groups present in highest concentration on the basal plane, and carboxylic acid groups around the periphery of the sheets.

Graphite oxide can be directly exfoliated in different solvents, inorganic (typically water^{157, 158}) or organic^{159, 160} (such as DMF, PC, and NMP), by mechanical force (such as ultrasonication which may fragment the platelets reducing their lateral dimensions by over an order of magnitude down to a few hundred nanometers, or stirring which may reserve much larger lateral dimensions and aspect ratio, however, very slow and in low yield) to form colloidal suspensions of graphene oxide (GO)¹⁶¹. Zeta potential measurements indicate that these suspensions are electrostatically stabilized by negative charges, possibly from the carboxylate groups that are believed to decorate the periphery of the lamellae¹⁵⁸. GO is likely to maintain the chemical structure of graphite oxide – highly hydrophilic and often described an electrical insulator due to the disruption of sp^2 bonding networks. GO is typically characterized by C/O ratios of approximately 2¹⁴⁴.

Rapid heating^{12, 162, 163} and microwave radiation¹⁶⁴ can exfoliate and reduce graphite oxide to yield products which have been correspondingly called thermally expanded graphite oxide (TEGO) and microwave-expanded graphite oxide (MEGO). These products, however, are indeed functionalized graphene. "TEGO" and "MEGO" are still used in the following description for correspondingly obtained graphene with a purpose to highlight the functionalization process. In the thermal expansion and reduction process dry graphite oxide powder is typically subjected to thermal shock, i.e., exposure to a sudden jump in temperature up to that such as 400°C or higher at high heating rates such as 2000°C/min^{158, 162}. The rapid heating is believed to cause various small molecule species, e.g., CO, CO₂, water, to evolve thus increase internal pressure forcing the sheets apart and yielding a dry, high-surface area (700-1500 m²/g) material with a low bulk density. TEGO (reported C/O ratio of ~10¹⁶²) is electrically conductive (reported conductivity value of ~2000 S/m¹⁶²). It was also reported

that TEGO contains residual oxygen (in the form of carbonyl and ether groups) and adopted a crumpled accordion-like morphology, with lateral dimensions of a few hundred nanometers, similar to GO platelets exfoliated by sonication^{162, 165}. MEGO has a C/O ratio of $\sim 3^{164}$ and is also electrically conductive (reported conductivity values of roughly 270 S/m¹⁶⁴).

Other reported chemical modification methods include: covalent modification for the preparation of organomodified GO by amidation of the carboxylic groups^{166, 167} (using different organic amines to reduce the hydrophilic character of GO by forming amide and carbamate ester bonds with the carboxyl and hydroxyl groups, respectively); non-covalent functionalization of reduced graphene oxide $(rGO)^{153-155}$ in the presence of polymer or polymeric anions resulting in a stable polymer-grafted dispersion of graphene; nucleophilic substitution to epoxy groups¹⁶⁸ using a reaction of amine with an aqueous dispersion of GO to prepare aliphatic amine-modified GO; and diazonium salt coupling¹⁶⁹ reducing GO with hydrazine followed by functionalization with aryl diazonium salts hence the functionalized graphene can be dispersed readily in *N*,*N*-dimethylformamide (DMF), dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP) up to 1 mg/ml with minimal sedimentation.

An example of so-called electrochemical modification was reported by Liu et al¹⁷⁰ in which graphite rods as electrodes were immersed in a phase-separated mixture of water and imidazolium-based ionic liquids under a constant potential of 10-20 V. Ionic liquid functionalized graphene sheets originating from the graphite anode precipitated after 10 minutes electrochemical reaction, which, after being dried, can be dispersed in DMF by ultrasonication resulting in a homogeneous suspension (1 mg/ml) with a layer thickness of ~ 1.1 nm.

A Canadian company, NanoXplore, developed commercial products of low-functionalized and partially oxidized graphene by a mechanochemical exfoliation method (proprietary and patent protected graphene production technology). A ball-mill method (shear forces) is used to exfoliate the graphene, and an oxidizing agent, solvent and surfactant to partially oxidize the graphene and add functional groups¹⁷¹. Such graphene is edge-functionalized with hydroxyl, epoxy and carboxyl groups to encourage interaction at the edges with target material(s), which is hence not hydrophilic and unable to be dispersed in water.

6.3. Characterization of graphene as raw materials and in polymeric composites

Fast and accurate characterization of morphology and surface properties of graphene in purchased or prepared products – dry powder, suspension, masterbatch, deposit or (nano)composite, is very important for scaling up the production and for the quality control of graphene related materials. A pre-study¹⁷² and a summarized guide of graphene characterization¹⁷³, which especially provide available characterization resources across Sweden, have been published on SIO Grafen's website (www.siografen.se).

6.3.1. Graphene particles

6.3.1.1. Layer number, platelet size and morphology

Optical contrast of graphene layers on different substrates is the most simple and effective method for the identification of the number of layers. This method is based on the contrast arising from the interference of the reflected light beams at the air-to-graphene, graphene-to-dielectric, and (in the case of thin dielectric films) dielectric-to-substrate interfaces¹⁷⁴. The optical image in Figure 5 reveals the difference of graphene with 1, 2, 3 and 4 layers on Si substrate using contrast spectra generated from the reflection light of a white-light source¹⁷⁵. A total colour difference (TCD) method, based on a combination of the reflection spectrum calculation and the International Commission on Illumination (CIE) colour space was developed to investigate quantitatively the effect of light source and substrate on the optical imaging of graphene for determining the thickness of the flakes¹⁷⁶.



Figure 5: Optical image of graphene with 1, 2, 3 and 4 layers (Reprinted with permission from Ref. [175], Copyright 2007, American Chemical Society)

In **Scanning Electron Microscopy** (**SEM**), the secondary electron intensity from the sample operating at low electron acceleration voltage has a linear relationship with the number of graphene layers¹⁷⁷; a quantitative estimation of the layer thickness can be obtained using attenuated secondary electrons emitted from the substrate with an in-column low-energy electron detector¹⁷⁸.

Transmission Electron Microscopy (TEM) can be directly used to observe the number of layers based on viewing the edges of the sample – each layer corresponding to a dark line; the relative intensities of the electron diffraction patterns from the {2110} and {1100} planes can be used to differentiate single from multiple layers of graphene – if $I_{(1100)}/I_{(2110)}$ is >1 it is

reported as single-layered graphene, and if the ratio is <1 it is multi-layered graphene^{179, 180}; high-resolution TEM (HR-TEM) can identify atomic bonds on functionalized sheets (C-OH vs C-O-C) and atomistic defects^{181, 182}, and has confirmed the existence of aliphatic islands containing oxygen bonded carbons¹⁸³.

AFM can be used to obtain the morphological feature and probe the thickness of graphene layers; from the steps of graphene on substrate, it is also possible to estimate the number of graphene layers^{140, 141, 184}.

UV-visible spectroscopy can also be used for determination of the number of graphene layers based on the fact that the transmittance of graphene decreases with increased layers: each graphene layer is 97 % transparent, while bilayer graphene is 94.3 % transparent and six-layer graphene 83 % of at the same wavelength¹⁸⁵.

6.3.1.2. Structural, chemical and electronic characteristics of graphene

The pristine graphene and single-layer GO shows absorption at 262 nm and 230 nm in the **UV-visible spectrum**, respectively, due to the π - π * transitions of aromatic C-C bonds. rGO also has less transparency compared with GO, which is attributed to the recovery of sp^2 carbons to restore electronic conjugation in reduced graphene¹⁸⁶.

Pristine graphite shows a basal reflection (002) peak at 2θ =26.6° (some literatures reported 26.3°) in the **X-ray diffraction (XRD)** pattern. After oxidization the (002) peak shifts to a lower angle at 2θ =13.9° (some literatures reported 14.1°-14.9°) due to the existence of oxygen functionalized group and water molecules in between the layers^{186, 187}. Disappearance of the diffraction peak can indicate that the sheets of GO exfoliate into single sheets^{188, 189}.

X-ray photoelectron spectroscopy (XPS) can quantify the amount of oxygen on the surface and also identify the types of carbon oxygen bonds. Chemical shifts in XPS C₁s spectra can be evidence for existence of C-O, C=O, or O-C=O on GO and its derivatives but are limited in quantifying their relative amounts^{190, 191}. ¹³C NMR may be the most direct method to distinguish oxygen functional groups. However, since the NMR-active ¹³C allotrope occurs naturally at only ~1 %, signal-to-noise ratio is low^{187, 192}.

Raman spectroscopy has been extensively used to probe the structural and electronic characteristics of graphene¹⁷⁶. Figure 6 shows typical Raman spectra of 1-, 2-, 3- and 4- layered graphene prepared using micromechanical cleavage technique and placed on SiO₂/Si substrate. The Raman spectrum of graphene has three major bands¹⁹³.



Figure 6: Representative Raman spectra of 1-, 2-, 3-, and 4-layered graphene prepared using micromechanical cleavage technique and placed on SiO2/Si substrate: (left) Raman spectra as a function of the number of layers, and (right) zoom-in view of the Raman 2D-band. (Reprinted with permission from Ref. [175], Copyright 2007, American Chemical Society).

• <u>The G band</u>: is a sharp band that appears around 1587 cm⁻¹ in the spectrum of graphene, which is an in-plane vibrational mode involving the *sp*² hybridized carbon atoms that comprised the graphene sheet. The G band position is highly sensitive to the number of layers as defined empirically in equation 1.

$$\omega_G = 1581.6 + 11/(1+n^{1.6}) \tag{1}$$

where ϖ_G is the band position in wavenumbers, and *n* is the number of layers present in the sample. The intensity of the G band also follows a predictable behaviour that can be used to determine graphene thickness. The intensity of this band follows closely a linear trend as the sample progresses from single to multilayer graphene. The G band intensity method will be less susceptible to the effects of strain, temperature and doping compared to the G band position method, therefore may provide a more reliable measurement of layer thickness when these environmental factors are present.

• <u>The D band</u>: is known as the disorder band or the defect band that would appear at around 1350 cm⁻¹ if any. The band is typically very weak in graphite and typically

weak in high quality graphene. The intensity of the D band is directly proportional to the level of defects in the sample, e.g., a significant D band means a lot of defects in the material.

• <u>The 2D band</u>: is the second order of the D band appearing at around 2700 cm⁻¹, but it does not need to be activated by proximity to a defect. Hence the 2D band is always a strong band in graphene even when there is no D band present, and it does not represent defects. This band is also used to determine graphene layer thickness, which depends not only on band position but also on band shape. For single-layer graphene the 2D band is observed to be a single symmetric peak with a full width at half maximum (FWHM) of ~30 cm⁻¹. Adding successive layers of graphene causes the 2D band to split into several overlapping modes. These distinct band shape differences allow the 2D band to be used to effectively differentiate between single and multilayer graphene can also be identified by analyzing the peak intensity ratio of the 2D and G bands. The ratio I_{2D}/I_G for high quality (defect free) single layer graphene will be seen to be equal to 2.

However, traditional characterization techniques which estimate the quality of the graphene material using the intensity ratio between the D and the G peaks are unreliable for GO, rGO and functionalized graphene^{194, 195, 196, 197}. The existence of D' band (~1620 cm⁻¹) with sufficient concentration of defects is one of the possible explanations for the shift of G band in the Raman spectra of GO to higher frequencies (blue shift). The superposition of the G and D' band gives rise to an apparent G peak, the G_{app}^{195} . King et al.¹⁹⁵ defined a second-order transition, 2D' (~ 3200 cm⁻¹) shifting by as much as 40 cm⁻¹ from GO to rGO, and furthermore, three types of graphene derivatives from the Raman spectra, see equation (2) – (4):

$$GO = D'_{inf} - G_{app} < 0; C/0 < 10$$
(2)

$$rGO = 0 < D'_{inf} - G_{app} < 25; 10 < C/0 < 500$$
(3)

$$G_{graphene} = D'_{inf} - G_{app} > 25; C/O > 500$$
 (4)

where D'_{inf} is the inferred D' mode. They suggested that the amount of reduction can be predicted from the energy difference between the G_{app} and D' or 2D' peak.

6.3.2. Graphene dispersions/deposits

A lot of studies have relied on the changes of physical properties to demonstrate the dispersion of graphene and interactions between graphene particles and between graphene and polymer matrix. These indirect methods will be particularly reviewed in the following chapters in combination with composites processing. In this section, the techniques that can

measure directly the graphene in suspensions, on fibre reinforcement and in composites will be briefly reviewed.

6.3.2.1. Microscopic characterization

SEM, **TEM** and **AFM** are commonly used to characterize the morphology of graphene modified materials, such as graphene coated fibres or polymers, and polymer/graphene dispersions. Sample preparation is a critical aspect when using these techniques, which will either make available the information required, or obscure it by distorting the native structure of the sample thus producing 'artefactual' or 'spurious' images.

TEM gives information that will be imaged at the same time on a single plane, so will give the most accurate information regarding the morphology (nanoplatelet dimension and stacking layers, etc.) of graphene in different matrices. When graphene is in solutions they must be dispersed as thinly as possible (mono-dispersed being ideal) on carbon film coating rids before characterization. For characterization of bulk/solid materials, such as graphene/polymer, the materials need to be sectioned to < 100 nm. Kim and Macosko measured statistically the particle thickness defined by a full width at half-maximum, and aspect ratio A_f defined by the ratio of the lateral dimension to the thickness based on TEM images⁵ (Figure 7).



Figure 7: TEM micrographs of poly(ethylene naphthalate) (PEN) with (a) and (b) 3 wt % graphite and (c) and (d) 3 wt % functionalized graphite sheets (FGS, by rapid thermal treatment on oxidized graphite), and the shape distribution of graphite and FEG from TEM analysis (Reprinted with permission from Ref. [5],Copyright 2008, American Chemical Society)

SEM is used to generate information from the surface of 'bulk' samples in contrast to TEM. The surface of materials can be imaged 'as is', or after being fractured in liquid nitrogen. Therefore, SEM can be a powerful tool to correlate processing-structure-properties of graphene modified composites. The SEM images in Figure 8 demonstrates a strong anisotropy of graphene nanoplatelets alignment and uniformity of distribution along LDPE flow in the extrusion direction, and different dispersion efficiency by using compression screw and mixing screw, respectively, for processing the nanocomposites¹⁹⁸. The fracture surfaces of epoxy with the addition of graphene and flame retardant⁸⁴, which were obtained from composites after bending test, indicate clearly that graphene has strong mechanical interlocking with epoxy chains, leading to a much rougher fractured surface relative to epoxy and epoxy/flame retardant composite.

The SEM images were also taken to show the surface morphology of GO-doped carbon fibres (CFs) and PP fibres, respectively. The influence of ultrasonication on enhancing the quality and quantity of GO deposition on CFs during electrophoretic deposition (EPD) process was clearly shown¹⁹⁹. The enhancement of hydrophily of PP fibres by plasma treatment, higher doping efficiency achieved by electrophoresis than by simple dipping process, and more agglomerate by higher concentration of GO suspension for fibre coating were well reflected in the SME images (Figure 9)²⁰⁰.



Figure 8: SEM images of freeze-fractured surfaces of melt compounded LDPE/graphene nanocomposites with 1 wt% (a and c) and 5 wt% graphene (b and d): (a and b) when a compression screw was used during the extrusion; (c and d) when a mixing screw was used during the extrusion, where the extrusion direction is indicated by circles (Reprinted with permission from Ref. [198])



Figure 9: SEM images with different magnifications of PP/GO nonwovens fabricated by dipping or electrophoresis process: (a) M-PP/GO-1-dipping, (b) PP/GO-1, (c)-(d) M-PP/GO-0.5, (e)-(f) M-PP/GO-1, and (g)-(h) M-PP/GO-2. Note that M-PP means 'plasma treatment modified PP nonwoven', and the number after GO is the concentration of GO aquepus suspension (g/l) (Reprinted with permission from Ref. [200], Copyright 2015, Spring Nature).

AFM has a lateral resolution similar to that of a Field Emission Gun SEM (FEGSEM), however, is ideally suited to explore variation in sample surface detail along the Z plane.

6.3.2.2. XRD

XRD is used to characterize the levels of exfoliation/intercalation of graphene layers in composites. PLA/graphene and PLA/rGO nanocomposites were prepared by melt blending with the assistance of plasticizer, respectively. PLA caused a wide diffraction from 10° to 25°. A sharp diffraction at 26.6° associated with graphitic (002) plane was observed in all PLA/graphene nanocomposites, which, however, was not observed in the nanocomposites with rGO. This attributed to the fully exfoliated graphitic layers of rGO, which were not reassembled or re-aggregated when rGO was incorporated into PLA matrix. Such a XRD pattern indicated that the rGO still existed in a single graphene layer and exfoliated in PLA matrix, which was further confirmed in the TEM images²⁰¹.

The XRD spectra of pristine PP, plasma treatment modified PP, GO and GO doped plasma-modified PP²⁰⁰ is shown in Figure 10. The graphene was successfully oxidized based on the intensity and diffraction angle of the peak at approximately 10.6° representing the interlayer spacing of GO nanosheets. Four distinct diffraction peaks appeared at 2θ value of 14.159°, 16.747°, 18.026° and 21.324° corresponding to the (100), (040), (130) and (131) crystal planes diffraction peaks of PP, respectively. The plasma-modified PP/GO showed a weak peak at 9.17° which responded to the characteristic peak of GO at 10.6°. This peak shift to left in combination with weaker peak intensity may be attributed to the crystallization

behaviour of PP crystal. The XRD results also indicated that plasma treatment had no effect on the structure of PP nonwovens, and GO nanosheets were successfully assembled on the modified PP nonwovens.



Figure 10: XRD spectra of GO, PP, plasma treatment modified PP and plasma-modified PP/GO nonwoven. (Reprinted with permission from Ref. [200], Copyright 2015, Spring Nature).

Additionally, the degree of crystallinity can also be obtained from the diffractograms, which has important influence on controlling the physicochemical properties of the thermoplastic based material²⁰².

6.3.2.3. Fourier transform infrared spectroscopy (FTIR) and XPS

The combination of these two techniques can usually provide accurate information of the functionalization of graphene and how the interactions between graphene and polymer matrix are influenced. An example, in a work related to butadiene-styrene-vinyl pyridine rubber (VPR)/functionalized graphene (GO coagulated by CaCl₂ or HCl) nanocomposites: the shift to higher wavenumber of the peak (FTIR) due to the CN bond indicates the presence of hydrogen bonding, and the new peak at 1608 cm⁻¹ assigned to the protonated pyridine group (-CNH⁺) confirms the ionic bonding; the downshift of the two species in the composite samples suggests the hydrogen bonding between GO and VPR (XPS) and the presence of the third peak for the HCl functionalized GO composite indicates the presence of N⁺ providing evidence of an electrostatic interaction between the negatively-charged GO and N⁺ of the VPR²⁰³.

6.3.2.4. Raman spectroscopy

The test samples for Raman spectroscopy characterization can be flat surface sectioned from composites.

Graphene nanoplatelets with average particle diameter of 5, 15 and 25 μ m were melt compounded with PP, respectively, with different loadings, to prepared the nanocomposites followed by injection moulding²⁰⁴. All PP/graphene composites show D, G and 2D bands of the spectrum located at ~1335, ~1585 and ~2750 cm⁻¹, respectively. The combination of neat PP spectrum and graphene particles spectrum at each composite can be seen in Figure 11. The location of D band increased with increasing graphene loading. At 2D band, the location of Raman shift decreased. At higher graphene loading, the exhibited effect of PP was lower possibly due to the high modulus of graphene.

In highly conductive few-layer graphene (FLG)/epoxy nanocomposite, the G and 2D peaks of FLG were dominated in Raman spectra of graphene-rich regions, while the most representative of epoxy (i.e., E Peak ay ~1610 cm⁻¹) was more prominent in the Raman spectra of epoxy-rich regions. The intensities of both G and 2D peaks could be used to map the spatial distribution of FLG in the polymer matrix²⁰⁵.



Figure 11: Raman spectrums for neat PP and PP/graphene nanoplatelet (with different nanoplatelet diameter and loadings, respectively) composites prepared by melt compounding followed by injection molding. (Reprinted with permission from Ref. [204)

6.3.2.5. Rheology

Rheology can be an effective tool for quantifying nanocomposite dispersion and nanoparticlepolymer adhesion, determining the rheological percolation thresholds (using linear and nonlinear viscoelastic oscillatory shear tests)²⁰⁶, and predicting processability. In the rigidity percolation regime where the shear storage modulus, *G*', becomes independent on frequency at low frequency, the concentration ϕ dependence of the elasticity of particle suspensions can be described by power law scaling^{207, 208}:

$$G' \propto (\phi - \phi_{perc})^{\nu} \tag{5}$$

where ϕ_{perc} is the percolation threshold and v is a power-law exponent, which can be determined experimentally from a plot of low-frequency G' versus ϕ - ϕ_{perc} .

Viscoelasticity measurement of LDPE/graphene nanocomposites at 140°C (at melt state) was performed to study the impact of graphene loadings, the morphology and the formation of particle network within the nanocomposites²⁰⁶. In linear conditions, there was no clear evidence of the existence of an additional elastic contribution at the lower frequencies

although the moduli increased slightly with increasing graphene content in the whole frequency range that was recorded. In contrast, the presence of a percolated network was shown in nonlinear conditions using frequencies that did not disclose such behaviour in linear viscoelastic measurement. However, the correlation between the melt rheological behaviour and mechanical, thermal and barrier properties of the nanocomposites was not demonstrated in this study.

6.4. Global leading graphene producers and their products

Table 2, Table 3 and Table 4 summarize some leading graphene producers worldwide including their key technologies and main products that are promising for composites applications. The supplier guide published on SIO Grafen's website can also provide supplemental information²⁰⁹.

6.4.1. Europe

Table 2:	Leading	graphene	producers	in	Europe
14010 2.	Leaung	graphene	producers	in	Latope

Company	Location	Key technologies	Products	Comments
Haydale (https://www.hay dale.com/)	UK	A patented HDPLAS® low temperature plasma process to produce functionalized graphene with enhanced surface engineering (to add specific chemical groups and remove non crystalline structures), without acid treatment (not using chemical acid treatment to avoid damage and degradation of functional performance, structural integrity and mechanical strength)	 Three specific graphene enhanced CF prepregs using functionalized graphene dispersed in epoxy resin formulations for enhanced electrical conductivity (lightning strike protection, EMI and RFI shielding), thermal conductivity (for dissipation of heat) and mechanical performance (modulus/wear resistance) Joint research with Huntsman Advanced Materials for graphene masterbatch with ARALDITE[®] epoxy resins (ARALDITE[®] epoxy resins (ARALDITE[®] Euremelt hot melt resin aimed for prepreg market, and a general purpose epoxy resin used in many composite processes) 	A press release can be found in 2016, but commercial products cannot be found on Haydale's website.
Versarien (AIM:VRS) (<u>http://www.versa</u> <u>rien.com/</u>)	UK	 Patented method to manufacture high quality, independently verified, few- layer graphene (2-DTech Ltd acquired in 2014) Patented processes to manufacture novel graphene inks (Cambridge Graphene Ltd acquired in 2016) 	 graphene oxide, reduced graphene oxide, graphene nanoplatelets, dry large graphene nanoplatelets (all in powder form, available in any quantity, from 2-DTech Ltd) Proprietary graphene inks (from Cambridge 	Versarien buys ACC Cyroma (specialist plastic manufacturer) to make the first dedicated graphene

			Graphene Ltd)	plastic manufacturing factory in the world
Graphenea (<u>https://www.gra</u> <u>phenea.com/</u>)	Spain		- Graphene oxide: 1) G-O water dispersion (0.05 wt %, 0.4 wt% and 2.5 wt %, monolayer content >95 %) and powder (dispersible in polar solvents), 2) reduced graphene oxide (chemically reduced, low- concentrations (<0.01 wt%) dispersability in NMP, DMSO, DMF), 3) graphene oxide film (diameter of 4 cm and thickness of 12-15 μm, non-conductive) by filtration of a monolayer graphene oxide dispersion - CVD graphene film on different substrates, such as polymer film, Cu, PET, PEN, quartz, etc.	A partner of the Graphene Flagship
Avanzare (<u>http://graphene.a</u> <u>vanzare.es/</u>)	Spain		 Pristine graphene, GO (power and water dispersion), highly (oxygen content below 2.5 % and up to 3.5%) and partially reduced graphene oxide, graphene nanoplatelets Graphene thermoplastic masterbatch based on TPU, LDPE, PA6, with 0.1 wt% GO Functional industrial masterbatch – high conductive, based on TPU, PA6 and PP Filaments (diameter of 1.75 – 3 mm) for 3D printing based on PLA, TPU 	A highly reputed company in the graphene sector, and one of the main drivers of the leading international Research and Development project GRAPHENE FLAGSHIP
Advanced Graphene Products Sp. Z 0.0.(AGP) (https://advanced grapheneproducts .com/)	Poland	Two main methods to produce large-area graphene: - CVD - Metallurgical (HSMG [®]) to manufacture large-area polycrystalline graphene sheet with a metallurgical method based on graphene liquid phase growth, i.e., crystallized on a liquid metal surface which allows each graphene particle to rotate and rearrange until fitting perfectly into the	 High strength metallurgical graphene (HSMG[®]) much stronger and durable than CVD graphene (double tensile strength): tensile elongation 100%, single and multilayer sheets of any size Graphene oxide water dispersion (0.05 wt %) Graphene oxide film Reduced graphene oxide powder 	

		crystallizing graphene sheet therefore has little to no imperfections	- CVD graphene on available substrates: Cu, PET, quartz, SiO ₂ /Si, SiC, PMMA	
2D Fab AB (<u>http://2dfab.se/</u>)	Sweden	A proprietary fluid mechanical exfoliation method	- customized graphene	
GraphMaTech (<u>http://www.grap</u> <u>hmatech.com/</u>)	Sweden	A novel and patented ionic graphene nanocomposite material (hybrid graphene- lithium salt)	Aros Graphene [®] ionic graphene nanocomposite material applicable in form of powder, film on a substrate and suspension	
Abalonyx (<u>http://www.abal</u> <u>onyx.no/</u>)	Norway	A new scalable process (modified version of the Hummers method)	- graphene oxide (acidic and acid-free) suspensions, freeze-dried powder and film - reduced graphene oxide	
Akkolab LLC (<u>http://www.akko</u> <u>lab.ru/en/</u>)	Russia	Reduction of graphene oxide produced using modified Hammers method	- Graphene and graphene oxide in powders (flakes): flake size 0.2-1.5 μm/1 atom-layer in dispersion/no more than 10 atom-layers in powders - Graphene dispersion in water and in organic solvents (on request, such as chloroform, DMA, TGF, etc.): 0.4 wt%	The only company in Russia producing and supplying graphene whose characteristics aren't inferior and even superior to their foreign analogues
Applied Graphene Materials (AGM, previously Durham Graphene Science) (<u>http://www.appli</u> <u>edgraphenemateri</u> <u>als.com/</u>)	UK	Graphene nanoplatelets (A- GNPs) are produced through a proprietary and scalable, bottom-up synthesis process	- A-GNPs - Graphene dispersions: graphene in a wide range of solvents (water, DMSO, MEK, xylene, IPA, etc.), thermoplastics (HPVA, HDPE, EVA, LDPE, PP, PS, PA and ABS, etc.) and thermosets (low-medium viscosity epoxy resin, vinyl ester resin, PTFE, PU, etc.) upon request	
BGT Materials Limited (previously BlueStone Global Tech) (<u>www.bgtmateria</u> <u>ls.com</u>)	UK		- Well-exfoliated mono and few-layer graphene with large aspect ratio or predominantly monolayer - Graphene oxide water suspension (with predominantly single- layer G-O, prepared using a fully environmentally friendly method, oxygen content 30%)	
Cambridge Nanosystems (<u>https://cambridg</u> enanosystems.co	UK		 Graphene and graphene oxide powder CamGraph[®] Graphene dispersions in either a 	

		deignized distilled water	
<u>III/</u>)		defonized distined water	
		or isopropanol solvent	
		- CamGraph [®] conductive	
		resin with matrix of	
		Araldite LY556 and XB	
		3473	
Directa Plus	Italy	Water based dispersions	
(http://www.dinee	Italy	- water-based dispersions	
(<u>nttp://www.direc</u>		of pristine graphene	
<u>ta-plus.com/</u>)		nanoplatelets up to 20	
		wt% and no oxidation	
		process is involved (one	
		can be without surfactant)	
		- Extremely fine pristine	
		graphene nanoplatelets	
		- Masterbatch of pristine	
		graphana nanoplatalata (70	
		graphene nanoplatelets (70)	
		wt%) in a polyolefin	
GrapheneTech	Spain	- Graphene nanoplatelets	
(http://www.grap		in powder form (2-10	
hene-tech.net/)		layers)	
		- Graphene dispersion in	
		different solvents (water	
		IDA THE athylana	
		grycol, ethanol, etc.) with	
		a wide range of	
		concentrations from 0.01	
		to 3 wt%	
		- Masterbatch based on	
		different thermoplastics	
		I I I I I I I I I I I I I I I I I I I	
		(HDPE LDPE PP PS	
		(HDPE, LDPE, PP, PS, Polyamide 6, PVC)	
Cranhitana		(HDPE, LDPE, PP, PS, Polyamide 6, PVC)	
Graphitene	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder	
Graphitene (<u>www.graphitene.</u>	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC) - Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized water 	
Graphitene (<u>www.graphitene.</u> <u>com</u>)	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized water 	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized water 	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u>	UK	 (HDPE, LDPE, PP, PS, Polyamide 6, PVC) Graphene oxide powder Reduced graphene oxide powder Graphene nanoplatelets powder Silane-modified graphene powder Alkylamine functionalized graphene powder Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent, or IPA-based solvent (0.05 wt %) Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized water Elicarb[®] Graphene series products: 	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u>	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few-	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u> <u>swan.co.uk/chemi</u>	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u> <u>swan.co.uk/chemi</u> <u>cal_products/elic</u>	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and graphene nanoplateletes	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u> <u>swan.co.uk/chemi</u> <u>cal_products/elic</u> <u>arb/</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and graphene nanoplateletes - Graphene/plastic	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u> <u>swan.co.uk/chemi</u> <u>cal_products/elic</u> <u>arb/</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and graphene nanoplateletes - Graphene/plastic masterbatches upon	
Graphitene (<u>www.graphitene.</u> <u>com</u>) Thomas Swan (<u>http://www.thom</u> <u>as-</u> <u>swan.co.uk/chemi</u> <u>cal_products/elic</u> <u>arb/</u>)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and graphene nanoplateletes - Graphene/plastic masterbatches upon request	
Graphitene (www.graphitene. com)	UK	(HDPE, LDPE, PP, PS, Polyamide 6, PVC)- Graphene oxide powder - Reduced graphene oxide powder - Graphene nanoplatelets powder - Silane-modified graphene powder - Alkylamine functionalized graphene powder - Graphene-monolayer (<5% oxygen) dispersion with NMP/DMF-based solvent, or IPA-based solvent (0.05 wt %) - Graphene oxide (oxygen: 35-45 %)-monolayer dispersion: 0.4 wt % in deionized waterElicarb® Graphene series products: - Highly conductive few- layer graphene and graphene nanoplateletes - Graphene/plastic masterbatches upon request - Graphene/enoxy	

			dispersion 15%	
CealTech (<u>http://www.cealt</u> <u>ech.com/</u>)	Norway	A patented and commercialized 3D graphene production (based on David Boyd's techniques as per Nature communications, (DOI: <u>10.1038/ncomms7620</u>) using an industrial-scale, plasma- enhanced chemical vapor deposition (PE-CVD) reactor, FORZA TM	 vertically grown PE- CVD graphene: few- to very few-layered, high purity, with properties comparable to those of pristine graphene at the industrial scale commercialized graphene-modified products and solutions for composites & coatings, energy storage, and healthcare 	 Production is planned from January 2018 Participated projects regarding composites: graphene- based anti- corrosion coating; graphene- based elastomers, pains, isolation materials, fibre glass, epoxies and resins

6.4.2. America

Table 3: Leading graphene producers in America

Company	Location	Key technologies	Products	Comments
NanoXplore (http://www.nano xplore.ca/)	Canada	Edge-functionalized (partially oxidized) high-grade graphene powder produced by a mechanochemical exfoliation method based on patents (2 granted US patents and 3 pending patents) such as: https://www.google.com/paten ts/US9586825	 Graphene powder: GrapheneBlackTM 3X with 6-10 layers and peak decomposition temperature at 750°C, insoluble Graphene-enhanced plastics including masterbatch: thermoplastic/graphene masterbatch pellets based on PE (LDPE, LLDPE and HDPE), PP, PC, ABS, PET, PS, PLA, where the graphene content varies between 15-35 wt%; thermoset/graphene masterbatch based on epoxies (3 epoxy resins – Epon 826, KER 828 and Heloxy 48, compatible with LY556 resin) can be used for masterbatch with graphene content of 20-30 wt%), siloxanes and rubber formula 	Very prompt and detailed reply when contacted and high-quality service
Graphenemex (<u>http://graphenem</u> <u>ex.com/</u>)	Mexico		 Graphene Graphene oxide Reduced graphene oxide CVD graphene Developing graphene- 	Information of graphene- enhanced polymer composites

		enhanced polymer composites including masterbatches in pellet form	cannot be found in the website
ACS Material (https://www.acs material.com/)	United States	It has various types of graphene products and the most amazing ones that are very promising for composites are listed below: - Single layer graphene: prepared by completely reducing graphene oxide (prepared by the modified Hummer's method), which is conductive (electrical resistivity \leq 0.30) and can be redispersed in many solvents with the help of sonication - Graphene dispersion in NMP (with and without oxygen reduced, with dispersant, 0.1 wt %, 0.4 wt% and 4 wt %) - Graphene oxide (single- layer powder; high-surface area powder; DI water dispersion without surfactant) stable for more than 1 year	
Angstron Materials (<u>https://angstron</u> <u>materials.com/</u>)		 Graphene oxide aqueous dispersion: 0.5 wt% and 1.0 wt% Custom Graphene dispersions: using any of their graphene materials into a range of solvents by selecting the type of graphene, the concentration of solution and the volume of material required Graphene oxide with oxygen content 10-30% Pristine and polar graphene powder with oxygen content 1-4 % Graphene enhanced nanocomposites (masterbatch) available based on PP/PA6, PA66,PA12/PLA/PBT/H DPE/LDPE/LLDPE/ABS 	
AzTrong	United	- Graphene oxide and	

(http://www.aztro	States with	reduced graphene oxide	
<u>ng.com/</u>)	a 100-ton		
	production		
	facility in		
	Taiwan		

6.4.3. Asia

Table 4: Leading graphene producers in Asia

Company	Location	Key technologies	Products	Comments
XFNANO	China	Top-down and bottom-up	- Graphene with high	R&D and
(http://en.xfnano.		methods for production of	quality: graphene powder	manufacture
<u>com/</u>)		graphene and related	(chemical method -	focus on
		products (more than 20	monolayer with a	graphene,
		related IPs); can produce	thickness of 0.8-1.2 nm,	CNT and
		high quality single-layer	and physical method –	molecular
		graphene of 10 kg/day, few-	single layer ratio ~80%,	sieves
		layer graphene of 200	layer thickness ~0.8 nm);	
		kg/day, and graphene	graphene oxide (powder,	
		dispersion of 3 tons/day	flake (single-layer ratio:	
			(1.5 lowers)); corboxyl	
			(1-3 layers)), carboxyr	
			dispersion single laver	
			ratio: ~80%): aminated	
			graphene (TEPA	
			covalently linked	
			piperazine covalently	
			linked. amino-PEG	
			covalently linked and	
			octadecylamine covalently	
			linked); reduced graphene	
			oxide powder, etc.	
			- CVD graphene on	
			different substrates, such	
			as	
			copper/nickel/SiO ₂ /glass/p	
			lastics (e.g. PET), etc.	
			- Defect-free single	
			crystals of graphene	
			- Graphene-like materials,	
			e.g. phosphorus, boron	
			nitride, etc.	
	<u> </u>		- Graphene quantum dots	
2DM	Singapore	Top-down liquid extoliation	- premium quality	
(<u>https://2dmsoluti</u>		method	graphene with large-scale	
<u>ons.com/</u>)			production	
Carbon Nana	South Vorac		Multi lavar granhana (?	
Motoriol	South Korea		- Multi-layer graphene (3-	
Technology			10 layers)	
(http://www.corb				
onnano co kr/engl				
ish/english htm)				
NanoGrafen	Turkey		- Functionalized graphene	

(<u>http://www.nano</u> <u>grafen.com.tr/en</u> <u>index.html</u>)		powder with different C/O ratio - Graphene oxide - Graphene masterbatch based on PP, HDPE, epoxy hardeners and new formulations according to the needs of customers - Graphene oxide partially soluble in water, homogeneous dispersion in DMF, THF, other organic polar solvents and epoxy hardener (oxygen content ≤4 % so reduction is assumed to happen)	
NanoGrafi (<u>https://nanografi.</u> <u>com/graphene/</u>)	Turkey	 Graphene and graphene oxide Graphene sheet 29 cm x 29 cm Graphene sheet 29 cm x 59 cm 	First time to see the graphene sheets with large scale
The Sixth Element Materials (<u>http://www.c6th.</u> <u>com/graphene/</u>)	China	- Graphene water suspension (8 wt %) - Graphene NMP suspension (4 wt %)	

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