Mechanical properties of graphene and graphene-based nanocomposites

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Abstract

In this present review, the current status of the intrinsic mechanical properties of the graphene-family of materials along with the preparation and properties of bulk graphene-based nanocomposites is thoroughly examined. The usefulness of Raman spectroscopy for the characterization and study of the mechanical properties of graphene flakes and their composites is clearly exhibited. Furthermore, the preparation strategies of bulk graphene-based nanocomposites are discussed and the mechanical properties of nanocomposites reported in the literature are analysed. In particular, through the analyse of several hundred literature papers on graphene composites, we have found a unique correlation between the filler modulus, derived from the rule of mixtures, and the composite matrix. This correlation is found to hold true across a wide range of polymer matrices and thus suggests that the common assumption that the filler modulus is independent of the matrix is incorrect, explaining the apparent under performance of graphene in some systems. The presence of graphene even at very low loadings can provide significant reinforcement to the final material, while the parameters that affect the nanocomposite strongly are thoroughly reviewed. Finally, the potential applications and future perspectives are discussed with regard to scale up capabilities and possible developments of graphene-based nanocomposite materials.

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Abbreviations: ABS, acrylonite butadiene styrene; ATP, attapulgite; CB, carbon black; CF, carbon fibres; CHI, chitosan; CHIGEL, chitosan/gelatin; CNT, carbon nanotubes; Co(OH)2, cobalt hydroxide; CTBN, carboxy terminated butadiene acrylonitrile; EPDM, ethylene propylene diene monomer; EVOH, poly(ethylene vinyl alcohol); fGNP, functionalized graphene nanoplatelets; fMWCNT, functionalized multiwalled carbon nanotubes; fGO, functionalized reduced graphene oxide; GF, glass fibres; GN, graphene nanosheets; GNP, graphene nanoplatelets; GNR, graphene nanoribbons; GO, graphene oxide; Gr, graphene; HDPE, high density polyethylene; IIR, poly(butylene-co-isoprene); KGM, konjac glucomannan; LLDPE, linear low density polyethylene; MMT, montmorillonite; MVQ, methyl-vinyl-silicone (silicone rubber); MWCNT, multiwalled carbon nanotubes; NR, natural rubber; OPBI, poly[2,2′-(p-oxodiphenylene)-5,5′-bibenzimidazole]; OPE, oxidized polyethylene; PA6, polyamide 6; PBS, poly(butylene succinate); PC, polycarbonate; PDMS, polydimethyl-siloxane; PEG, polyethylene glycol; PET, poly(ethylene terephthalate); PF, phenol formaldehyde; PHO, polyhydroxyoctanate; PIM, polyimidide; PLA, polylactic acid; PMA, poly(methyl methacrylate); PP, polypropylene; PS, polystyrene; PSF, polysulfone; PTFE, polytetrafluoroethylene; PTM, poly(trimethylene terephthalate-block-tetramethylene oxide) copolymer; PU, polyurethane; PVA, poly(vinyl acetate); PVC, poly(vinyl chloride); PVDF, Poly(vinylidene fluoride); PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene); rGO, reduced graphene oxide; SBR, styrene butadiene rubber; SCF, sized carbon fibres; SiO2, silicon dioxide; SR, silicone rubber; TPU, thermoplastic polyurethane; UHMWPE, ultra-high molecular weight polyethylene; VMQ, vinyl-methyl-silicone rubber; WPU, waterborne polyurethane; XNBR, carboxylated acrylonitrile butadiene rubber.
## 1. Introduction

Seven years after the award of the Nobel Prize in Physics and thirteen years since the first report [1] of freestanding, monolayer graphene, the worldwide interest in this “wonder material” is still increasing, as can be realized from the number of publications per year and the massive investment in research. The reason for this interest is mainly due to the multifunctionality of this 2D-atomic crystal which combines unique properties such as thermal conductivity in the order of 5000 W/C K [5], high electron mobility in room temperature (250,000 cm²/V s) [3], large surface area (2630 m²/g) [4], high modulus of elasticity (∼1 TPa) [5] and good electrical conductivity, making it attractive for use in a vast number of applications. The list of potential applications includes high-end composite materials [6,7], field effect transistors [8], electromechanical sys-
Graphene, “the mother of all graphitic forms of carbon”, is a single layer of carbon atoms that are held together by a backbone of overlapping sp² hybrid bonds [23]. The extraordinary characteristics of graphene originate from the 2p orbitals, which form the π state bands that delocalize over the sheet of carbons that constitute graphene. As a result, graphene is extremely stiff, exhibits very high thermal conductivity, has zero effective mass, is impermeable to gases, displays high mobility of charge carriers, while it is optically transparent [24]. All these properties give graphene a comparative advantage over similar materials that have been used in different applications. As a result, there is a need for high-quality graphene in bulk quantities for both industry and academia, in order to cover the demands of the parties involved and propel the material into commercial applications. For this reason, several preparation strategies have been proposed in literature and a number of them are already employed by companies supplying graphene.

2. Graphene
2.1. Properties-characteristics

Graphene, “the mother of all graphitic forms of carbon”, is a single layer of carbon atoms that are held together by a backbone of overlapping sp² hybrids bonds [23]. The extraordinary characteristics of graphene originate from the 2p orbitals, which form the π state bands that delocalize over the sheet of carbons that constitute graphene. As a result, graphene is extremely stiff, exhibits very high thermal conductivity, has zero effective mass, is impermeable to gases, displays high mobility of charge carriers, while it is optically transparent [24]. All these properties give graphene a comparative advantage over similar materials that have been used in different applications. As a result, there is a need for high-quality graphene in bulk quantities for both industry and academia, in order to cover the demands of the parties involved and propel the material into commercial applications. For this reason, several preparation strategies have been proposed in literature and a number of them are already employed by companies supplying graphene.

2.2. Preparation routes and scale-up

2.2.1. Mechanical exfoliation

Mechanical exfoliation is the simplest of the preparation methods and surprisingly is the method that made stand-alone graphene a reality and led to Geim and Novoselov being awarded the Nobel Prize in 2010 [25]. In this technique, a piece of graphite undergoes repeated tape exfoliation and is then transferred to a substrate. The number of layers can then be evaluated with different methods; by using a simple optical microscope, Raman spectroscopy, atomic force microscopy and/or scanning tunnelling microscopy. This preparation method still makes the highest quality crystals, but is only useful for lab-scale experiments and prototyping as it is not possible to scale-up the process.

2.2.2. Chemical vapor deposition (CVD)

CVD is one of the most useful methods to prepare monolayer graphene of high structural quality for use in different devices [26]. Large area samples can be prepared by exposing a metal to different hydrocarbon precursors at high temperatures. There are different types of CVD methods available such as plasma-enhanced CVD, thermal CVD, hot/cold wall CVD and many others. The exact mechanism of the formation of graphene depends on the growth substrate but typically initiates with the growth of carbon atoms that nucleate on the metal after decomposition of the hydrocarbons and the nuclei grow then into large domains. Apart from gaseous hydrocarbons such as methane, ethylene or acetylene, liquid precursors have also been used such as hexane [27] or pentane [28] while the quite diverse set of materials that can be used for the CVD production of graphene can even include food, insects and waste [29]. The transfer of graphene from the growth substrate to a substrate of interest can be difficult due to the chemical inertness of graphene and it can attribute defects and wrinkles to the material, while the thermal fluctuations can also affect the stability of the grown material [30]. Moreover, the com-

Two major tables summarizing the reinforcing effect of graphene-based materials in a number of polymer matrices have been constructed, while the study of the Raman band shifts for bulk nanocomposites has also been evaluated.
plectomy of the CVD process and the high energy demands for the specific method add to the difficulties of the task, but CVD still remains one of the most successful methods for large-area graphene production.

In terms of upscaling, CVD is a viable candidate for the production of high-quality graphene in large area quantities and for this reason several research groups have focused their attempts towards this direction. One of the first attempts was the one from Bae et al. [31] who used a roll-to-roll (RTR) process for the production of 30-in. graphene films and subsequently the RTR technique was successfully applied for the continuous production of graphene [32–36]. In a similar recent report by Polsen et al. [37], graphene was once again produced by a RTR process using a concentric tube CVD. Lin et al. [38] developed a surface engineering method and succeeded in producing cm-size single-crystalline graphene by passivation of the active sites and control of graphene nucleation by using melamine pretreatment of the Cu surface. Moreover, a really promising and different attempt by Bointon et al. [39] recently produced high-quality monolayer graphene by using resistive-heating cold-wall CVD, that was also 100 times faster than conventional CVD. Despite the promising results reported from these and similar studies, the mass production of graphene by CVD has predominantly focused on the electronic device industry.

A very interesting method for the production of inch-sized single-crystalline graphene has been proposed by Wu et al. [40]. The authors applied a controlled nucleation method on a Cu-Ni alloy, by locally feeding carbon precursors to a desired position. According to the authors, the use of the specific alloy activated an isothermal segregation mechanism, which resulted in higher growth rates. The final material that they obtained was high-quality, 1.5-in. single crystalline graphene, which was synthesized in 2.5 h and exhibited a Hall mobility of 10,000–20,000 cm² V⁻¹ s⁻¹ at room temperature.

2.2.2. Liquid phase exfoliation

Liquid phase exfoliation is another method used widely for the production of graphene and it involves three different steps: (1) dispersion in a solvent or surfactant, (2) exfoliation and (3) purification in order to separate the exfoliated material from the non-exfoliated and, if supplied as powder, completely remove any solvent traces [41,42]. Initially studies used ultrasonic to exfoliate graphite flakes in a suitable solvent, such as NMP [43]. Sonication time is very important since higher concentrations of graphene can be achieved by longer sonication times, at the expense of energy consumption. Following the sonication step, the material is composed of thicker flakes, which can be removed by ultracentrifugation. Higher centrifugation speeds result in thinner flakes but with a small lateral size, that are not so useful for applications such as composites. A variety of liquids can be used for the dispersion of graphene, including aqueous surfactants. The output of this process can be estimated from the yield by single-layer graphene percentage, which has been defined as the ratio of the number of single layer flakes to the total number of graphic flakes in the dispersion. The yield can be adjusted by altering the starting amount of graphite, the sonication time and the rotational speed of the centrifuge amongst other parameters. The problems that are related with the specific process include the electrical properties of produced graphene which can be similar to the ones of graphene oxide as a result of poor transport at contacts between the graphene sheets [44]. Additionally, the use of highly-reactive solvents can increase the cost, while the process itself is potentially not ecologically-friendly as a large amount of solvent has to be used due to the very low solubility of the graphene.

Liquid-phase exfoliation is one of the most promising techniques for the upsampling of graphene production. The simplicity, speed and high throughput that are associated with this process make the specific route attractive for the mass production of graphene. A key advance was from Paton et al. [45] who showed that high shear forces can be used rather than ultrasonic cavitation and thus exfoliated graphene on a 100 litre scale. The critical shear rate for the exfoliation of graphene was found to be ~10⁴ s⁻¹, which can be achievable even from conventional kitchen blenders. Following centrifugation, the mean number of layers was found to be less than 10, while the typical lateral sizes of the nanosheets were in the 300–800 nm range. However, it should be noted that the yield achieved was relatively low and the choice of starting material along with the optimization of the rotor can strongly affect the exfoliation efficiency. Recently, Dimiev et al. [46] prepared graphene nanoplatelets over a 3–4 h time period, at room temperature and the conversion yield from graphite to GNPWs was almost 100%. Due to the existing industrial knowledge and equipment, liquid exfoliation is possibly the most viable option for upsampling graphene production, however as Ciesielski and Samori have pointed out in their review [43], it is critical to standardize the procedure and define a reproducible protocol, relying on the key parameters of the process. This will be a major step towards the simplification of the process which is definitely needed in order to make it applicable for industry.

2.2.4. Electrochemical exfoliation

The specific approach includes the use of a liquid solution (electrolyte) and an electrical current which is used to consume an electrode consisting of graphite. This process takes place via anodic oxidation or cathodic reaction of the graphite-based electrode. Cathodic reaction methods are more suitable for the production of high-quality few layer conductive graphene for use in energy and optical applications [47]. On the other hand, anodic oxidation is more widely reported in the literature. The resulting anodic material consists of several graphene layers, has a low yield and resembles graphene oxide in terms of its oxidation state, in contrast to pristine monolayer graphene [48]. The advantage of electrochemical exfoliation over the other methods is that the process takes place via a single step, which makes it easier to operate, while it proceeds over a period of minutes/hours, in contrast to most methods which demand longer times for the preparation and stabilization of the final material. A very important parameter for nanocomposites is the lateral size of the flakes produced, which depends on the graphite source and the conditions of the intercalation-exfoliation process. The products of intercalation with non-oxidative salts can reach a lateral size of 50 µm with a thickness of 2–3 layers [49]. Moreover, the use of liquid electrolytes
or aqueous surfactants makes the process eco-friendly, while interestingly, this method can be used to produce a product very similar to graphene oxide (GO), with the use of LiClO₄ as an electrolyte [50], avoiding the dangerous and toxic chemicals used in most GO preparation methods.

The electrochemical route can offer potential for scaling up the production of graphene due to all the advantages mentioned above, however there are several drawbacks that should be additionally considered. The ionic liquids used in some routes are expensive, while the crumpled morphology of graphene that can be produced may limit its applications [51].

2.2.5. Chemical reduction of graphene oxide

Chemical reduction involves the exfoliation of graphene oxide into single-layer GO sheets, followed by the in-situ reduction of the GO for the production of graphene-like monolayers. This process is strongly affected by the choice of the solvent, the reducing agent and the surfactant, which are combined in order to maintain a stable suspension. The quality of the material produced cannot be considered high since it contains both intrinsic defects (such as edges or deformations) and extrinsic defects (such as O- and H-containing groups), therefore it is debatable if the material produced can be properly classified as graphene. Various reducing agents can be used such as hydrazine monohydrate [52] (which is the most common in the early literature), hydroquinone [53], sulphur-containing compounds [54] and others [52,55]. The elimination of the oxygen-containing groups from GO demands strong reduction ability but the process should not leave traces that may affect the final product. The use of environmentally-friendly approaches, such as L-ascorbic acid [56], has been followed over the past few years due to the need to avoid the use of strong chemicals [57–61]. Such methods have the advantage of the processability of the material in different solvents or the relatively easy scale up of the process. On the other hand, the use of environmentally-friendly solvents does not quite yield graphene with a quality as high as that prepared by hydrazine, while the production of the initial GO product involves the use of equally strong and hazardous chemicals, which ought to be minimized during this process. Moreover, thermal reduction of GO can be performed using a fast heating rate, under an inert gas and high temperatures (up to 1000 °C). The efficiency of the process depends on the pressure generated from the heating

![Fig. 1. The key characteristics of the most common graphene production methods in a scale of 0–3; (G) refers to the graphene quality, (C) refers to the cost of production (a low value corresponds to high cost of production), (S) refers to the scalability, (P) refers to the purity and (Y) refers to the yield of each preparation route. Reproduced with permission from [47]. Copyright 2015, Nature Publishing Group.](image-url)
procedure that counteracts the van der Waals forces that are present between the graphene sheets and facilitates exfoliation of the flakes [62,63].

The produce of graphene-like material from the reduction of GO has the potential to be scaled up, similar to liquid phase exfoliation, however the chemical inhomogeneity of GO along with the inevitable generation of defects during the oxidation process can lead to difficulties.

2.2.6. Bottom-up synthesis

An alternative method to synthesize graphene is the bottom-up approach, where graphene molecules are prepared starting from small and atomically-precise building blocks [64]. These building blocks need to have coupling sites that can be stimulated externally in order to assemble to the next structural units. The process usually takes place at high temperatures where the structural variants are produced and then some of them are separated in order to yield the intended structure. The major advantage of this method is the atomically precise control of resolution that results in very high quality graphene. Müllen and coworkers have worked extensively on the production of nanographene and graphene nanoribbons by applying a bottom-up synthesis. The GNRs synthesized were usually relatively long (>200 nm), could be processed in liquid phase and were chemically precise, with various edge and width structures, that could further enhance their processability and find application in wider research areas, such as polymer nanocomposites [65–71]. A drawback of this method is the constraint in the handling and transfer of the material produced, along with the few possibilities for upscaling due to limitations of large-scale uniformity and order.

2.2.7. Summary of production methods

It is clear that intensive research efforts have been made over the last few years on the mass production of graphene, in order for it to be introduced into practical applications. Each production method attributes different characteristics to the final material and has different possibilities for upscaling. The advantages and the drawbacks of each method have been nicely summarized in a recent progress article by Raccichini et al. [47]. The authors also evaluated different graphene production methods in terms of the most important aspects of the graphene produced (quality and purity) and of each method (scalability, cost and yield). Their results are presented in Fig. 1. It can be seen that each method presents different characteristics in terms of the output and for this reason, the selection of the method should be performed each time, based on the...
application for which the graphene will be used. For example, the reduction of graphene oxide which is used extensively in the literature exhibits very high yield and possibilities for scalability; however the quality and purity of the material produced is quite low. Moreover, some liquid-phase exfoliation processes may have low yield but produce high quality graphene, and can be readily scaled up.

2.3. Characterization

The multifunctionality of graphene is one of the reasons why it can be readily characterized by a wide variety of experimental techniques. In terms of microscopy, the fact that it is very active optically, makes it possible to observe graphene in a simple optical microscope and even discriminate in this way flakes with different numbers of atomic layers (Fig. 2a). Ellipsometry can be also used for the evaluation of the number of layers, when the microscope contrast is not high enough [72]. The surface morphology and the respective wrinkles or folds can be observed with the aid of scanning electron microscopy (SEM), while the pioneering use of in situ SEM can provide insights into the dynamics of growth of graphene by CVD on a copper substrate [73] or by growth on a polycrystalline Ni substrate [74].

The atomic structure of graphene can be observed directly by transmission electron microscopy (TEM) (Fig. 2b) which is particularly useful for the evaluation of the different structures such as vacancy defects, bond rotations, dislocation edges, grain boundaries, layer stacking and other features [75]. Scanning tunnelling microscopy (STM) can provide information about the morphology and the electronic properties of graphene in three dimensions. Once again structural characteristics such as the defects, folds, periodicity, etc. can be fully evaluated [76,77] and it can be particularly useful for material on substrates, since STM can provide important information about the effect of the interface between the substrate and graphene [78–80].

Atomic force microscopy (AFM) is one of the most widely used techniques for characterizing the number of layers, since the original work of Novoselov et al. established that monolayer graphene is 0.4 nm thick [1]. The surface area of the samples can be measured by the Brunauer-Emmett-Teller (BET) method [81]. UV–Vis spectroscopy is also useful for the chemical analysis of graphene dispersions in different solvents since it enables monitoring of the reaction process [82] by using Beer’s law and the linear relationship between the absorbance and concentration of the solution. Moreover, X-ray diffraction (XRD) can be applied for the evaluation of the exfoliation and intercalation of graphite and the ultimate formation of graphene. The characteristic Bragg peak of graphite at $2\theta \approx 26^\circ$ broadens with decreasing number of layers, and it ultimately disappears for monolayer graphene. Scherrer’s formula can be also used for a relative estimation of the number of layers from an X-ray diffractogram. X-ray photoelectron spectroscopy (XPS) is commonly applied for the characterization of the surface chemical structure of graphene, especially for samples that have been chemically modified, by yielding the binding energy between the carbon-carbon and carbon-oxygen bonds in the material.

Finally, Raman spectroscopy is one of the most important methods used in the study of graphene and its derivatives. The intense resonant Raman scattering even from monolayer graphene provides a very strong signal for the material, while the differences in the spectra between materials with different number of layers, established Raman spectroscopy as a very convenient technique for characterization of the material. It has been recognized that the signature of monolayer graphene is the intensity of the 2D band (found at around 2700 cm$^{-1}$ depending on the excitation laser wavelength) which is at least twice the intensity of the G band (found at around 1560 cm$^{-1}$) (Fig. 2c) [83]. Interestingly, for two-layer graphene, the 2D band shifts to higher wavenumber, and the intensity of the 2D band is lower than that of the G band, while with increasing layer number 2D band broadens significantly and develops a shoulder, which is characteristic of many-layer graphene (graphite) (Fig. 2d). Furthermore, the Bernal stacking order of graphite in multilayer graphene, which is important for the overall performance of the material, can be evaluated by Raman spectroscopy [84,85].

2.4. Mechanical properties

2.4.1. Stiffness

The impressive mechanical properties of graphene are one of the reasons that make graphene stand out both as an individual material and as a reinforcing agent in composites. The reason for the exceptional mechanical properties of graphene

Fig. 3. (a) Illustration of the nanoindentation setup in a suspended monolayer graphene membrane, (b) loading/unloading curve with increasing indentation depth. From [5]. Reprinted with permission from AAAS.
lies in the stability of the $sp^2$ bonds that form the hexagonal lattice and oppose a variety of in-plane deformations. Hone and coworkers [5] first measured the mechanical properties of free-standing monolayer graphene by using nanoindentation in an AFM (Fig. 3a) and established graphene as "the strongest material ever measured", in their words. The authors used the force-displacement response from the graphene membranes in order to obtain both the elastic properties and the breaking stress of graphene. The force-displacement curves (Fig. 3b) were found to be insensitive to the tip radius, while contrarily, the breaking force mainly depended on the radius of the tip and it was independent of the membrane size. The maximum stress was obtained using the equation: 
\[ \sigma^{\text{RT}} = \frac{(E^{\text{RT}})^{1/2}}{C_3} \]
where $E^{\text{RT}}$ is the second order elastic stiffness, $R$ is the tip radius and $F$ is the applied force. However, the breaking strength of 55 N m$^{-1}$ which was calculated from this equation can not be considered accurate, since this model ignores nonlinear elasticity. After a series of numerical simulations, the relationship between the breaking force and the third-order elastic constant was established. The breaking force obtained experimentally and from simulation was almost identical and the experimental value of the second order elastic stiffness was equal to $E^{\text{RT}} = 340 \pm 50$ N m$^{-1}$. This value corresponds to a Young's modulus of $E = 1.0 \pm 0.1$ TPa, assuming an effective thickness of 0.335 nm.

Some reports, however, have obtained different values of stiffness, probably originating from the inherent and inevitable crumpling of graphene in the out-of-plane direction of monolayer. Crumpling emerges from either out-of-plane flexural phonons or from static wrinkling, which is caused by uneven stress at the boundary of the graphene produced and it is responsible for the deterioration of the mechanical properties of the material. Moreover, another possible origin of crumpling is the presence of point defects at a finite distance, such as the Stone-Wales defects [87]. In a recent report by Nicholl et al. [88] the authors developed a novel non-contact experimental approach based on interferometric profilometry, where both CVD and exfoliated graphene were pressurised electrostatically by applying a voltage between the membrane and the gating chip. The results showed that graphene is significantly softened by out-of-plane crumpling since the in-plane stiffness was found equal to 20–100 N m$^{-1}$ at room temperature. The results are in accordance with Ruiz-Vargas et al. [89] who also reported decreased stiffness of crumpled CVD graphene by using nanoindentation measurements. Crumpling and wrinkling are very important aspects of graphene and both play a major role on the design of complex nanomechanical systems. Buehler's lab has performed extensive research on the formation and fine-tuning of both by choice of substrate, surface tailoring and controlled folding and unfolding of graphene [90–93].

### Table 1

| Sample no. | Crack size $a_0$ (nm) | Fracture stress $\sigma_f$ (GPa) | $\sqrt{K_c}$ (MPa $\sqrt{m}$) | Stress intensity factor $K_c$ (MPa $\sqrt{m}$) |
|------------|-----------------------|-------------------------------|-------------------------------|-----------------------------------------------|
| 1          | 33                    | 9.51                          | 1.73                          | 3.1                                           |
| 2          | 438                   | 3.53                          | 2.34                          | 4.1                                           |
| 3          | 518                   | 2.87                          | 2.06                          | 3.7                                           |
| 4          | 600                   | 3.59                          | 2.78                          | 4.9                                           |
| 5          | 1256                  | 2.09                          | 2.34                          | 4.1                                           |
| **Average s.d.** |                     |                               |                               |                                               |
|            |                       |                               | 2.25                          | 4.0                                           |
|            |                       |                               | 0.35                          | 0.6                                           |

2.4.2. Strength

Defect-free, monolayer graphene is considered to be the strongest material ever tested, since Hone and coworkers measured the intrinsic stress of the monolayer membrane to be 42 N m$^{-1}$, which equates to an intrinsic strength of 130 GPa [5]. Zandiatashbar et al. [94] have studied the effect of defects on the intrinsic strength and stiffness of graphene. The defects were induced with a modified oxygen plasma technique, while AFM nanoindentation was used for the quantification of stiffness and strength of defective graphene. Furthermore, the defects were categorized as $sp^3$-type or predominantly vacancy type, based on the $I_D/I_G$ ratio of the Raman peaks, while the $I_D/I_G$ and $I_D/I_G$ were used for quantification of the level of defects. It should be noted here that the D- and D'-modes in Raman spectrum are caused by the disordered structure of graphene and they are activated by a single-phonon inter-valley and intra-valley scattering process. The G-mode is associated with the doubly degenerate phonon mode at the Brillouin zone center $E_{2g}$ while the 2D-mode originates from a double phonon scattering (either both on an electron-hole pair or on a single electron/hole) [95–97]. Interestingly, it was found that the strength and stiffness of graphene was maintained even at higher densities of $sp^3$-type defects, while the breaking strength is only 14% lower than the pristine graphene, in the $sp^3$-defect regime. Once the material passes into the vacancy-defect regime however, its strength drops significantly.

Qin et al. [98] used simulation in order to study the interlayer shear mechanical properties of wrinkled multilayer graphene and came into the conclusion that they are enhanced compared to its flat counterpart as a result of the geometrical locking effect. Different aspect ratios of wrinkled graphene were selected by tuning the topological defects in the graphene sheet. When an aspect ratio of $s = 0.77$ was selected, the shape of the wrinkled graphene remained the same during shear loading but the interlayer distance is changed, due to the fact that the flipping over deformation is harder and the preferred deformation mode is the separation between the two layers of graphene (upper/bottom). The authors defined the shear...
modulus as the secant modulus between the points of zero stress and peak stress (shear strength), i.e. \( G = \tau_s u_s / h_0 \) where \( u_s \) is the interlayer shear displacement at a point \( \tau_s \) and \( h_0 \) is the interlayer distance of the initial configuration. Therefore, adjusting the aspect ratio of wrinkled graphene at \( s = 0.177 \) gives a shear modulus of 1100 MPa and strength of 610 MPa, which are several times larger than flat graphene. The assembling of wrinkled graphene can lead to the preparation of a membrane with a tensile strength of over 12 GPa, as a result of its high interlayer shear modulus and strength. It should be stated though that the in-plane tensile modulus and strength of wrinkled graphene are both reduced due to the decrease of tensile stiffness of the wrinkled surface and the large residual stress that is concentrated on the defects of the material.

Wrinkling is an almost inevitable part of the transfer process of CVD graphene to a specific substrate and it is known to alter the mechanical stretchability [99] amongst other properties. Min and Aluru [100] performed shear test on zigzag graphene using molecular dynamic simulations in order to study the effect of wrinkles on the fracture stress. The authors found out that the fracture stress of flat graphene is 97.5 GPa, while that of wrinkled graphene is around 60 GPa at room temperature, as a result of the softening of the material due to the presence of the wrinkles.

2.4.3. Toughness
One of the most important mechanical properties of graphene is its fracture toughness, since it is a property very relevant to engineering applications. Zhang et al. [101] developed an in situ micromechanical testing device and a nanoindenter within a scanning electron microscope for the determination of the fracture toughness of CVD-synthesized graphene. The authors introduced a central crack in the graphene membranes using a focused iron beam (FIB) and brittle fracture was observed after applying a load. The fracture stress decreased with increasing crack length (Table 1) and the critical strain energy release rate \( (G_c) \) was found to be 15.9 \( \text{J m}^{-2} \), while the fracture toughness of graphene was measured as a critical stress intensity factor \( (K_c) \) of 4.0 ± 0.6 MPa. From this and similar works [102–105] it can be easily understood that the toughness of graphene, similar to most membranes, depends heavily on their weakest link where failure initiates. Addition-

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**Fig. 4.** (a and b) The C1s XPS spectra of GO and rGO. Reprinted from [52]. Copyright 2007, with permission from Elsevier. (c) XRD patterns of graphite, rGO and GO. Reproduced from [122] with permission from The Royal Society of Chemistry. (d) Thermogravimetric analysis (TGA) curves for GO and pyrolytic graphite (PG), along with the corresponding mass loss rate for GO. Reprinted (adapted) with permission from [123]. Copyright 2011, American Chemical Society. (e) AFM image of monolayer GO deposited in a SiO2 substrate. A folded edge is visible in the upper right part of the flake. Reprinted (adapted) with permission from [124]. Copyright 2007, American Chemical Society.
ally, in the numerous attempts to scale up the production of large graphene sheets, the accomplishment of this venture will probably result in a material that contains more defects, and therefore possesses inferior mechanical properties.

Buehler and coworkers used full atomistic simulations in order to investigate into the fracture mechanics of polycrystalline graphene, which is significantly affected by the mean grain size [102]. The fracture toughness of polycrystalline graphene was found to be 20–35% higher than that of pristine graphene due to the larger energy release rates (which decrease with increasing grain size). The theoretical results were in good agreement with experimental results such as the ones by Zhang et al. [101]. The authors found that the grain boundaries near a crack tip help distribute the stress, enabling deformation over a larger area. Moreover, the grain boundaries caused a branching of the cracks and create complex pathways, dissipating the energy even more throughout the material. The importance of the specific work from Buehler and coworkers lies in the demonstration that instead of the common perception that defects weaken graphene, the presence of grain boundaries on polycrystalline graphene can make it tougher than pristine graphene and can be a guideline for the preparation of CVD graphene with predictable toughness.

Several interesting routes have been followed for the exploration and utilization of the mechanical properties of graphene but one of the most unusual ones is the graphene-based shaped layers, inspired by Japanese kirigami [106]. Monolayer graphene was manipulated into springs that could be stretched by up to 240% of their initial length or twisted using a magnetic field without breaking. This idea could be extended in the future in order to construct high performance graphene-based mechanical metamaterials with microscale dimensions.

3. Graphene oxide

3.1. Preparation

Compared to monolayer graphene that is still considered to be a new material, graphene oxide, in the form of sheets of graphite oxide, has been known for more than 150 years, since Brodie attempted to determine the atomic weight of graphite by oxidizing graphite in potassium chloride and fuming nitric acid [107]. Later, Hummers [108] and Staudenmaier [109] modified the method of Brodie in an attempt to speed up the process of graphite oxide production while using less aggressive conditions, such as a mixture of sodium nitrate, concentrated sulphuric acid and potassium permanganate. The C/O ratio from both processes is similar (2:1) while they both introduce reactive oxygen functionalities to the original material. The structure of GO has been a subject of debate with respect to the presence and distribution of the oxygen functional groups and its nonstoichiometric atomic composition [110]. The presence of the oxygen groups affects the mechanical and electrochemical properties of GO strongly, compared to graphene. The utilization of these functionalities facilitates the excellent dispersion of GO in in water and different solvents which allows the facile preparation of polymer nanocomposites and the scale-up process for the production of GO in high volumes. On the other hand, the covalent oxygen functional groups in GO generate structural defects that in turn affect strongly properties such as the electrical conductivity, limiting the utilization of GO in electrically-conductive materials.

3.2. Characterization

Various spectroscopic techniques can be applied for the characterization of GO, including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Carbon-13 nuclear magnetic resonance (13C NMR), Raman spectroscopy and UV–VIS spectroscopy.

The XPS spectrum of GO (Fig. 4a and b) shows major differences compared to the one of graphene due to the evolution of the symmetric and narrow C1s band of graphene to a complex, broadened band, consisting of two maxima [111]. The oxygen functionalities are very obvious in the FTIR spectrum of GO, since multiple peaks at 3400 cm⁻¹ (O–H stretching vibrations), at 1720 cm⁻¹ (C=O stretching vibrations) and at 1060 cm⁻¹ (C–O stretching vibrations) amongst others, can be seen [112]. Moreover, the reduction efficiency can be evaluated from the intensity of the vibrations at the C–O and C=O peaks before and after the reduction process [82].

The 13C NMR spectrum of bulk GO has been used to study its structure and gives three characteristic peaks at 60, 70 and 130 ppm, assigned to C–OH, C–O–C and C=C=C groups [113]. The structural model that is most widely accepted is the one of Lerf, who used 13C NMR to characterize the material in detail [113]. Fully-oxidized GO exhibits an atomic C/O ratio of around 2:1, while it can form stable solutions. Alcohols and epoxides are its main functional groups, while carboxylic and ketone groups can be found on the edges of GO. Rourke et al. [114] have shown that GO that is prepared by the popular Hummers method, contains functional graphene sheets which consist of strongly-bound oxidative debris. The removal of the oxidative debris can be performed with a simple base wash, while the debris with higher levels of functionalization can be dissolved fully into water, leaving a suspension of functionalized graphene sheets. This process also enables deoxygenation, since it increases the C/O ratio [115].

The Raman spectrum of GO is also different than that of graphene, since a strong D band that is not present in graphene can be seen in GO, indicating the formation of the sp² bonds. There is also the broadening of the G band, compared to graphene. Moreover, the relative intensities of the G and D bands can be used for the evaluation of the defects that are formed during the reduction of GO [116]. UV–VIS spectroscopy can be also used for the evaluation of the GO dispersion and the study
of the reaction process. The electronic conjugation of GO can be assessed from the shifting of the characteristic peak at 230 nm towards higher wavelengths and the increasing of the intensity of absorbance, indicating the restoration of the conjugation [117]. Photoluminescence measurements are also important for the characterization of solutions of GO and especially base-washed GO. Thomas et al. [118] have shown that the oxidative debris of as-produced GO fluoresces much more intensely than the as-produced GO with a dispersive emission profile shifting to lower wavelength as the excitation wavelength is decreased and behaving as an ensemble of nanometre-sized fluorophores.

X-ray diffraction can be used to monitor the transformation from graphite to GO since the strong Bragg peak of graphite at (2θ = 26°) disappears after the conversion procedure and a new peak appears at lower angles (Fig. 4c). Moreover, the interlayer distance can be calculated with the use of Bragg’s law and generally ranges from 0.6 to 1.0 nm, depending on the preparation method. Thermogravimetric analysis is also useful since the presence of oxygen functionalities in GO enable the decomposition of the material at lower temperatures and in general, in three steps (Fig. 4d); the first one corresponds to the removal of moisture, the second one corresponds to the pyrolysis of the oxygen-containing groups and the third one is attributed to the decomposition of the more stable oxygen functionalities such as the carboxyls and phenols [119].

Several microscopy techniques have been used for the observation of the morphology of GO. Transmission electron microscopy (TEM) revealed that there are not any obvious differences with graphene in terms of its structure and electron diffraction pattern [120]. Scanning electron microscopy (SEM) showed its crumbled and randomly aggregated nature [52], while atomic force microscopy (AFM) (Fig. 4e) can be utilized for the evaluation of the exfoliation of the material in different solvents, along with the thickness of the flakes produced [121].

### 3.3. Properties of GO

As can be realized from the previous sections, the properties of GO do not outperform those of graphene, however due to its relative ease of fabrication in bulk quantities, GO still finds applications in composites, electronics, energy storage, biosensors, biomedicine and other areas. The disturbance of the sp² bonding, the presence of oxygen functionalities and the large number of defects reduce the electrical conductivity significantly (sheet resistance Rₛ values of about 10¹² Ω/sq [125]) and leads to poor thermal stability. The same picture emerges for the thermal conductivity of GO, since according to the work of Mu et al. the presence of oxygen even at a percentage as low as 5%, reduces the thermal conductivity by ~90% [126]. On the other hand, GO possesses excellent photoluminescence in the wavelength range from near-UV-to-blue visible to near-infrared [127] which is advantageous for biosensing or photoelectronics. Obviously, the chemical activity of GO is very high due to the presence of oxygen functionalities and defects and this is the main reason for the efficient reduction and functionalization of GO by different methods (see Section 2.2.5).

In terms of the mechanical properties of GO, the first report was published by Dikin et al. on a graphene oxide paper, assembled from individual GO sheets [128]. The stress distribution across the sample was homogeneous and the stiffness was found to be up to 40 GPa, while the strength was only 120 MPa. Several adjustments that have been subsequently proposed in the literature for the enhancement of the mechanical properties of similar materials [129–133] did not outperform significantly the initial values of Dikin et al. [128]. In an interesting report by Xu et al. [134], the authors produced continuous graphene fibres by wet-spinning of GO, followed by wet-drawing (a method where the GO dispersion is deposited in a coagulation bath and then the liquid crystalline fibres were drawn by a rotating drum). Ion cross-linking was also applied in this work since the use of divalent ions in the coagulation bath enables a construction of interlayer and intralayer crosslinking bridges between the oxygen containing groups, enhancing the mechanical properties of the fibres. The strength of the fibres produced was high, up to 0.5 GPa. More recent work on the production of GO fibres, reported results poorer or comparable to the ones of Xu [134] in terms of strength [135–137], while some reported enhancement of the Young’s modulus compared to GO paper [138]. The group of Gao have also researched extensively and produced impressive work on the formation, characteristics and properties of graphene oxide fibres (and hybrid graphene oxide fibres) [134,139–144] for applications such as supercapacitors [145–148], functional fabrics [149], stretchable conductors [150,151] and aerogels [152] amongst others.

The majority of research on the mechanical properties of GO has used conventional mechanical measurements under tension for the evaluation of the modulus and the strength of the materials. However, Gomez-Navarro et al. [153] utilized atomic force microscopy (AFM) for the evaluation of reduced GO sheets through tip-induced deformation. One layer thick rGO samples were suspended on a Si/SiO₂ wafer and the force versus piezo-displacement curves was recorded. The Young’s modulus of the GO sheets was calculated experimentally to be in the order of 250 GPa. In a similar report, Suk et al. [154] obtained the effective Young’s modulus of monolayer GO (thickness equal to 0.7 nm) with a combination of contact mode AFM and finite element method (FEM) of the order of 208 ± 23 GPa. Wang et al. [155] studied the deformation of a GO paper using in situ AFM in vacuum and in air. The failure stress of the GO paper micro-beams was lower under vacuum, since these conditions promote the removal of water between the layers, which leads to poor stress transfer and inferior tensile properties. Moreover, the authors identified a failure strength size dependency, since a decrease in specimen width, increased the failure strength of the GO paper.

Similarly to graphene, Raman spectroscopy has also been utilized for the evaluation of the mechanical properties of GO through the observation of the band shifts with increasing strain. Several literature examples of the application of the specific method for GO flakes are discussed in Section 5.4.
4. Standardization – nomenclature

The huge level of interest of the scientific and industrial community on graphene has led to a large number of research groups from all over the world working on “graphene” and “graphene-based materials”. Sometimes however, there seems to be a misunderstanding on the actual material that can really be named as graphene for different graphite-type derivatives. Several researchers use their own terminology, abbreviations and description to their materials, which can cause confusion to a non-experienced readership. The works of Bianco et al. [156] and Wick et al. [157] are an attempt to bridge this gap and categorize the graphene family members. These two papers should act as a guideline for the terminology of graphene in future work but also the researchers who undertake research on graphene and graphene-based composites should provide enough information in order to help the reader distinguish the type of graphene that has been used in each study.

According to the two publications, the three fundamental attributes of carbon-based two dimensional materials, are the number of layers, the C/O ratio and the lateral dimensions (Fig. 5). Based on those three properties, a classification of graphene-based materials can be performed. Initially, monolayer graphene is the one-atom-thick material in which sp2-bonded carbon atoms are hexagonally-arranged. Few-layer graphene is the material consisting of 2–5 sheets of graphene, while multi-layer graphene consists of 5–10 layers of graphene. Moreover, graphite nanoplatelets also consist of graphene sheets but their lateral dimensions/thickness are higher than those of many-layer graphene (more than 10 layers, less than 100 nm thickness). Finally, exfoliated graphite is a multi-layer material that can be prepared by partial exfoliation of graphite and retains its 3D crystal stacking.

Graphite oxide is produced from the oxidation of graphite using strong oxidizing agents, while graphene oxide originates from the exfoliation of graphite oxide using various methods (i.e. sonication). The C/O ratio of GO is typically 2:1–4:1 [158,159] and the same terminology that applies for the number of layers in graphene, can be used for GO. Moreover, reduced GO (rGO) is a material where after a reduction treatment, the oxygen content is significantly reduced, the C/O ratio can be improved up to 12:1 [160–162], while one report has presented a value as large as 246:1 [163].

5. Raman spectroscopy for the assessment of mechanical properties

As mentioned earlier, Raman spectroscopy is one of the most important techniques for the assessment of a number of important attributes and properties of the graphene family of materials. In this context, Raman spectroscopy can be applied to all carbon-based materials for the evaluation of their mechanical properties by the observation of the shift of characteristic bands when the material is under strain. With the application of strain, one can manipulate important characteristics of graphene, such as the optical response, its electronic structure and the chemical reactivity [164,165]. Fascinating phenomena have been observed so far by a number of groups when examining graphene under strain, such as the shifting of the Dirac
cones [166], superconductivity [167], enhancement of the electron-phonon coupling [167] and others [168]. The strain can induce shifts in the vibrational frequencies of the bands; therefore, this procedure can map the strain fields in flakes and composites with a high degree of precision. Tensile strain induces phonon softening (red shift), while compression induces phonon hardening (blue shift). The rate of shifting of photon frequencies under stress can be summarized in terms of the Grüneisen parameters, which can also provide information on the thermomechanical properties of the material [169]. Both fundamental and applied studies can be performed by measurement of the strain dependence of the Raman active phonons. The specific technique was initially developed by Young and coworkers for the deformation of carbon fibres [170] and was later successfully applied to carbon nanotubes [171,172] and graphene [169,173–181], while it can even be extended to different 2D materials such as MoS2 [182,183] and WS2 [184].

5.1. Uniaxial deformation of monolayer graphene

The first report of graphene flakes under strain was published by Ni et al. [174]. Tensile strain up to 0.8% was applied to mechanically exfoliated graphene and a red shift of the 2D and G bands were observed. The authors reported shifts of $-27.8 \text{ cm}^{-1}$/% and $-14.2 \text{ cm}^{-1}$/% for the 2D and G bands, respectively and attributed the phenomenon to elongation of carbon-carbon bonds. These shift values are significantly lower than those reported later. The reason for this can be the weak van der Waals forces between the polymer substrate and the flakes that did not prevent slippage of graphene during flexure. Slippage could only be avoided by applying the strain at small increments, so as to control the procedure and avoid loss of contact between the flake and the polymer. Moreover, the shifts of the 2D band of mono- and trilayer graphene were compared and it was found that the shift of trilayer graphene was lower, as a result of poorer stress transfer between the graphene layers. The high elasticity of graphene was revealed from the strain reversibility, since after the application of strain, the 2D band of the material returned to its initial position.

![Fig. 6.](image)

**Fig. 6.** (a) G and (b) 2D bands of monolayer graphene under uniaxial strain. The splitting of the G band can be observed for strain higher than 0.66% (indicated in the right side of the spectra). Reprinted (adapted) with permission from [169]. Copyright 2009 by the American Physical Society. (c) Evolution of the 2D band as a function of strain along the armchair and (d) the zigzag directions. Reprinted with permission from [186]. Copyright 2011 by the American Physical Society.
Mohiuddin et al. [169] also studied the Raman spectrum of graphene as a function of strain and observed a characteristic red shift and splitting of G* and G− peaks, while they realized that the 2D and 2D' bands also showed a downshift with increasing strain but did not split for small strains. Two- and four-point (uniaxial) bending setups were used and in the two-point measurements the spectra did not change up to 0.55% strain, while for the four-point bending, the downshift of the Raman bands evolved linearly from zero strain. The slope calculated for G* band was $-10.8 \text{ cm}^{-1}/\%$, for G− band was $-31.7 \text{ cm}^{-1}/\%$ and for 2D band was $-64 \text{ cm}^{-1}/(\%)$ (Fig. 6a and b). The different shift trends originate from their eigenvector orientations, where G* band is polarized perpendicular to the strain axis, while G− is polarized along the strain axis. The higher shifts of the G-band indicate that the elongated carbon-carbon bond is more sensitive in the direction along the strain axis. In this important work, the Grüneisen parameter ($\gamma_{G}$) was calculated for graphene. Under uniaxial strain the Grüneisen parameter is given by the equation:

$$\gamma_{m} = -\frac{1}{\omega_{m}^{0}} \frac{\partial \omega_{m}^{0}}{\partial \epsilon_{x}}$$

(5.1)

where the parameter $\epsilon_{x} = \epsilon_{||} + \epsilon_{\perp}$ is the hydrostatic component of the strain and $l$ and $t$ refer to the parallel and perpendicular directions of the applied strain. The parameters $\omega_{m}^{0}$ and $\omega_{m}^{0}$ correspond to the frequency of the phonons of peak $m$ at zero strain and in the presence of strain, respectively. Therefore, under uniaxial strain and given the fact that the G band is splitting into G− and G* components, the Grüneisen parameter ($\gamma_{G}$) and the shear deformation potential ($\beta_{G}$) can be obtained by:

$$\gamma_{\text{uniax}}^{G} = -\frac{\Delta \omega_{G}^{0} + \Delta \omega_{G}^{c}}{2 \omega_{G}^{0}(1 - v)\epsilon}$$

(5.2)

$$\beta_{G} = -\frac{\Delta \omega_{G}^{0} - \Delta \omega_{G}^{c}}{\omega_{G}^{0}(1 + v) \epsilon}$$

(5.3)

Moreover, the solution of the secular equation for the $E_{2g}$ mode is:

$$\Delta \omega_{E_{2g}}^{0} = -\omega_{E_{2g}}^{0} \frac{\gamma_{E_{2g}}}{1 - \gamma_{E_{2g}}} (1 - v) \epsilon \pm \frac{1}{2} \beta_{E_{2g}} \omega_{E_{2g}}^{0} (1 + v) \epsilon$$

(5.4)

where $v$ is the Poisson’s ratio. The above equations can also be adjusted for the D and D' bands in graphene and since the D band is not expected to split under uniaxial strain, only the hydrostatic component of the stress is taken into account. Moreover, the shear deformation potential cannot be obtained since the shear component of the applied uniaxial strain is missing. Therefore, the Grüneisen parameter for the specific bands takes the form:

$$\gamma_{\text{uniax}}^{D} = -\frac{\Delta \omega_{D}^{0} - \omega_{D}^{0}}{\omega_{D}^{0}(\epsilon_{||} + \epsilon_{\perp})}$$

(5.5)

The authors used Eqs. (5.2)–(5.4) and fitted them to the trends of the obtained band shifts with strain for the calculations of the Grüneisen parameter. In detail they found out that $\gamma_{G} = 1.99$, $\gamma_{D} = 1.61$, $\gamma_{D} = 3.55$ and $\beta_{G} = 0.99$ and the values were in good agreement with first principle calculations and with the ones obtained with density functional theory [185]. Yoon et al. [186] confirmed those findings in a later report, while the authors also observed the splitting of the 2D band of graphene at higher strains (up to 1.15%) along the armchair and zigzag directions (Fig. 6c). In contrast to the G band, the frequency shift rates for the 2D band were different from each other: $\partial \omega_{2D}/\partial \epsilon = -63.1 \text{ cm}^{-1}/\%$ and $\partial \omega_{2D}/\partial \epsilon = -44.1 \text{ cm}^{-1}/\%$ for the strain along the armchair direction, while $\partial \omega_{2D}/\partial \epsilon = -67.8 \text{ cm}^{-1}/\%$ and $\partial \omega_{2D}/\partial \epsilon = -26 \text{ cm}^{-1}/\%$ for the strain along the zig-zag direction, indicating that the direction of strain with respect to crystallographic orientation can play a major role on the shifts and the splitting of the bands.

Fig. 7. (a) Illustration of the biaxial strain apparatus and (b), (c) downshift of the G band of monolayer graphene with increasing strain during biaxial strain. Reproduced with permission from [189]. Copyright 2015, Nature Publishing Group.
The high flexural rigidity of graphene was confirmed shortly after Ni et al. [174] by Galiiotis and coworkers [176] who strained graphene on PMMA beams under tension (up to 1.3%) and under compression (up to 0.7%). The flakes were reported to undergo buckling at about 0.7% strain, indicating the flexibility of graphene. Slopes of around $-60 \text{ cm}^{-1}/\%$ at 0.9% strain were reported for samples under tension which demonstrates the ability of the flake to support the applied load. The results from the experiments under compression showed that $\partial \omega_{2D}/\partial \varepsilon$ diminished from an initial value of $+25 \text{ cm}^{-1}/\%$ to zero at 0.74% strain, which is an indication of residual strain. However, the fact that the graphene flake was uncoated on the polymer beam should be taken into account, since this makes it easier for the flake to become de-attached when compressive forces are applied.

Chen et al. [187] investigated graphene nanoribbons (GNRs) under uniaxial strains (0–6%) and used Raman spectroscopy in order to observe the shifts of the characteristic bands. In detail, the downshift of G band of nanoribbons with a width of 20 nm under strain exhibited a slope of $-10 \text{ cm}^{-1}/\%$. Moreover, the strain distribution was found to propagate from the middle and decreased towards the ends of the nanoribbons.

The formation of wrinkles during the transfer of CVD graphene to a specific substrate is almost unavoidable and it has a significant effect on the mechanical properties of the graphene. Li et al. [188] have shown that the microstructure of wrinkled CVD graphene consists of islands of monolayer graphene that are separated from the wrinkled material. By applying in-situ Raman with a bending procedure, the authors have showed that the shift rate of 2D band wavenumber per unit of strain was only $-12.8 \pm 2.0 \text{ cm}^{-1}/\%$, around 25% of that of flakes that had been mechanically exfoliated from graphite (60 cm$^{-1}/\%$). This has the result that the effective Young's modulus of wrinkled graphene is around 250 GPa, as opposed to almost 1 TPa for flat graphene. Similarly, the broadening rate of the 2D band was nearly 75% of that of un-wrinkled graphene. The small size of the graphene islands limits the reinforcing efficiency of the material (that is the capability to enhance or improve a property of the host matrix), and therefore causes a non-uniform strain distribution and lower rates of band shift.

### 5.2. Biaxial deformation of monolayer graphene

In contrast to uniaxial deformation which is most commonly used in these kinds of studies, Androulidakis et al. [189] subjected graphene flakes (ranging from monolayer graphene up to nanographite) to controlled biaxial deformation, a procedure that is important for thin films and membranes (Fig. 7a). The mean values of $\partial \omega_{2D}/\partial \varepsilon$ and $\partial \omega_{G}/\partial \varepsilon$ for a monolayer graphene membrane were found to be equal to $-148 \pm 6 \text{ cm}^{-1}/\%$ and $-62.3 \pm 5 \text{ cm}^{-1}/\%$ respectively (Fig. 7b and c), while the maximum strain that the membrane could withstand was almost 0.42%, at which point their PMMA cruciform broke. The Grüneisen parameters were calculated to be equal to $\gamma_{2D} \sim -2.86 \pm 0.12$ and $\gamma_{G} \sim -1.97 \pm 0.15$. Similar to the results from the four-point bending procedure [190], the shifts of the 2D and G bands of bilayer graphene were very close to the ones of monolayer with values in the range of $-155 \text{ cm}^{-1}/\%$ for the four components of the 2D band and $-57.2 \text{ cm}^{-1}/\%$ for the G band, while the increasing number of layers led to a reduction of the shift rates due to cohesive failure within the flakes.

Lee et al. also attempted to calculate the modulus of graphene by measuring the strain applied by pressure difference across a graphene membrane by Raman spectroscopy [191]. The graphene samples were exfoliated mechanically and deposited on a substrate patterned with round holes of different diameters. A pressure difference, which enabled a bulging of the sample similar to a balloon, was then introduced to the membrane after placing the specimens into a vacuum chamber. Raman spectroscopy was utilized for the estimation of the magnitude of strain by observing the shifts of the G and 2D bands; the Grüneisen parameter was taken to be equal to $\gamma = 2.2 \pm 0.1$ and the shear deformation potential was taken equal to $\beta = 0.93 \pm 0.04$. Therefore, the strain can be calculated by the equation $\Delta \omega_{2D} = -2 \omega_0 \partial \varepsilon / \partial x$ where $\omega_0$ is the frequency of unstrained graphene and $\varepsilon_x$ is the biaxial strain. The G peak shift of $\sim -13 \text{ cm}^{-1}$ for a hole with a diameter of 6.4 μm corresponds to a biaxial strain of $\sim 0.19\%$, while further investigations showed that the biaxial strain increases as a function of the size of the hole. The authors used a numerical simulation based on the finite element method and used the Young’s modulus as a fitting parameter in order to reproduce the measured strain at the center. They obtained a value of the Young’s modulus of monolayer graphene equal to 2.4 ± 0.4 TPa, while for bilayer graphene it was equal to 2.0 ± 0.5 TPa, which are amongst the highest values reported for the modulus of graphene. The reason for this is most probably the small strains that the authors applied on the graphene membranes, since the maximum strain was only 0.19%. The majority of literature on the modulus of graphene applied significantly higher strains, which are known to lead to a softening of the material, therefore a reduction of the modulus.

In an earlier report from Casiraghi and coworkers, the authors calculated the wavenumbers of the 2D band under uniaxial strain (0–6%) and used Raman spectroscopy to study the behaviour of the Raman spectrum of mono- and bilayer graphene [192]. The authors calculated the Grüneisen parameter from the equation: $\gamma = (\omega - \omega_0)/2 \omega_0$ where $\omega$, $\omega_0$ are the Raman frequencies at finite and zero strain and their calculations were in agreement with the values reported by Mohiuddin et al. [169]. In both mono- and bilayer graphene bubbles the small percentage of strain (1.2%) did not affect the stacking configuration, while it was realized that the doping or strain caused by the interaction of graphene with the substrate can heavily affect the Grüneisen parameters. Ding et al. also calculated the Grüneisen parameters for monolayer graphene subjected to tunable biaxial stresses (both tensile and compressive) with the aid of piezoelectric actuators [181]. In contrast with the work of Casiraghi and coworkers, the calculated Grüneisen parameters of the 2D and D bands were significantly different ($\gamma_{2D} = 2.3$ and $\gamma_{2D} = 2.98$) while a splitting of the D band was also observed. On the other hand, the calculated parameter for the 2D’ band was very close for both studies ($\gamma_{2D} = 1.61$).
Finally, Metzger et al. [177] performed measurements on graphene membranes deposited over a substrate patterned with shallow depressions, that revealed that the membranes did not remain free-standing but adhered to the substrate despite the biaxial strain induced. The calculated Gruneisen parameter for the 2D band was slightly higher than the ones presented by Mohiuddin et al. ($\gamma_{2D} = 3.8$ over $\gamma_{2D} = 3.55$) while a larger difference was revealed for the G band. It is clear that there is a range of values in the literature regarding the Gruneisen parameter, which as stated earlier is heavily affected by doping. Graphene on Si/SiO$_x$ substrate can be strongly doped as has been shown by Casiraghi et al. [193], while the presence of a water layer between the substrate and graphene can lead to strong p-doping [194].

5.3. Mapping of monolayer graphene

Jiang et al. [195] studied in detail the sliding and buckling of monolayer graphene on PET and observed the effect of the substrate during an uniaxial bending procedure. It was found that during loading, the interfacial stress transfer leads to tension in graphene, while the retraction of the PET surface during the unloading procedure imposes compression on the sample. The authors observed a red shift of the 2D band at a rate of $-52.5 \text{ cm}^{-1}/\%$ up to a strain of $\approx 1.2\%$. A nonlinear shear-lag analysis was applied on the data since the conventional shear-lag theory cannot predict the stress/strain distributions after the interfacial sliding of graphene at critical stress levels. According to this, the strain at which the measured Raman shift reaches a plateau value can be considered the plateau strain ($\epsilon_p$) at the center of the flake and it can provide the interfacial shear strength ($\tau_x$): $\epsilon_p = (\tau_x \cdot L)/(2 \cdot E_{2D})$ where $L$ is the length of the flake in the x-direction and $E_{2D}$ is the in-plane stiffness (or 2D Young’s modulus) of monolayer graphene. Moreover, it was found that the strain builds up from the edges and approaches a peak at the center of the flake, where the strain applied is equal to the strain of the substrate (up to 1.2% strain) (Fig. 8). For small strains, the strain distribution can be predicted by the classical shear-lag effect. The linear strain distribution around the edges which can be seen in Fig. 8, is evidence of interfacial sliding with a constant shear stress in the interface. The onset of sliding can be seen at a critical strain of $\epsilon_c \approx 0.3\%$, which is considered to be very low and most probably originates from the small dimensions of the flake under study. On the other hand, upon unloading, the interfacial shear stress is initially relaxed and then reversed in opposite directions, continuously compressing the graphene. Buckling ridges were observed at a compressive strain of $\approx -0.7\%$ and their number increased with increasing strain.

Raju et al. [10] followed the strain in the graphene/PMMA sensor coatings followed using Raman spectroscopy. They found out that CVD graphene coatings could read the strain in any 5 µm spot in the coatings, with an accuracy of 0.01% strain and resolution of about 27 microstrains, which is comparable with current commercial photoelastic systems. The authors realized that mechanically-exfoliated graphene exhibited no residual stress, while the CVD transferred graphene was in compression following solvent evaporation during its transfer although the residual stress relaxed after the first 2–3 deformation cycles. The shift rates of mechanically-exfoliated graphene were also 35% higher than the ones of CVD graphene, indicating that it is more sensitive, however the strain sensitivity of CVD graphene is still quite impressive. The effective modulus of both materials was obtained from the shift rates, and it was found in the order of $0.93 \pm 0.1$ TPa for exfoliated graphene and $0.52 \pm 0.12$ TPa for CVD graphene. Trung et al. [196] prepared strain sensors based on reduced GO field effect transistors (rGO-FET) that were found to detect strain at extremely low levels, as low as 0.02%, and showed excellent reliability under repeated mechanical deformation. Additionally, there are reports of the use of graphene as strain sensor in bulk composites, such as woven fabrics [197–199], elastomers [200–202], thermoplastics [203] and hybrids [204].

From the above, along with the fact that graphene is highly stretchable and almost transparent, it can be realized that the use of graphene can lead to high-performing strain sensors and there are several reports of its use in such applications. Most
of these original studies have dealt with monolayer graphene prepared either by mechanical exfoliation or CVD transfer. The strain devices were actually model graphene composites or graphene deposited in a specific substrate [205–209] from which the gauge factors were obtained.

5.4. Graphene oxide

In situ Raman spectroscopy has been also applied for studies regarding the load-bearing capability and modulus determination of GO, despite the limitations that the material presents, such as the absence of the 2D band, its crumpled nature and the presence of functional groups that are known to damage the graphene lattice. Another issue of concern for the specific experiments with GO is that the functional groups can make the material more vulnerable to damage from the laser beam, since it can undergo heat- or photo-reduction. In a report from Gao et al. [208], the authors modified a GO paper by introducing glutaraldehyde and water molecules into the gallery regions. The G band of GO was fitted with the respective G+, G, and D bands. The shift rates of the G+ and G bands were monitored as function of strain for the neat and the modified GO papers. The modified GO paper showed shifts in the range of \(-27 \text{ cm}^{-1}/\%\) for G+ and \(-14.6 \text{ cm}^{-1}/\%\) for the G band. The effective modulus was calculated in our previous review [22] by using the shift observed for the same band in monolayer graphene [169] and taking into account the thickness of the GO material. The effective modulus was found equal to 230 GPa, in accordance with the values obtained from Suk et al. [154] and Gomez-Navarro et al. [153].

Li et al. [211] recently analysed the deformation micromechanics of GO with continuum mechanics in order to evaluate the role of interlayer adhesion in GO and the effect on the reinforcement of nanocomposites. In general, the reinforcement from GO is enhanced from the presence of the functional groups which allow the occurrence of stronger interactions, better dispersion and stress transfer. However, the functional groups tend to damage the graphene lattice and increase the interlayer thickness, which reduces the intrinsic stiffness by a factor of 4, compared to pristine graphene [154]. Therefore, there should be an optimal degree of functionalization to maximize the reinforcement from GO. The authors [211] came into the conclusion that the number of GO layers does not affect the reinforcement efficiency of GO; consequently the degree of exfoliation will not affect heavily the ultimate mechanical properties of the composites. The fact that the number of layers also does not affect the Raman spectrum of GO makes the specific analysis more difficult, especially when GO flakes are deposited on a polymer beam. The authors applied strain (up to 1%) and observed the downshift of the D band as a result of the elongation of the C–C bonds. Up to 0.4% strain, the slope of the downshift of the D band was \(-14.9 \text{ cm}^{-1}/\%\), while from that point on the slope decreased as a result of partial interfacial failure or variation of the Gruneisen parameter with strain [212] (Fig. 9a). Another important finding presented in this work was that during the study of the strain distribution in a GO flake, the strain was kept constant with position along the flake (Fig. 9b), while for pristine graphene the strain falls over several micrometers to zero near the edge of the flake, allowing the determination of “critical length” for reinforcement. The critical length \(l_c\) is an important parameter, dependent on the strain distribution along the flake and it appears to be constant for the case of GO. As a result of the weak Raman scattering of GO, the poor resolution of the GO edges under the microscope and the spatial resolution of the Raman laser itself (1–2 \(\mu\)m), critical lengths of around 1–2 \(\mu\)m are difficult to measure.

6. Model nanocomposites

The majority of fundamental studies on the mechanical properties of graphene were upon freestanding graphene membranes prepared either by mechanical exfoliation of graphite or by CVD methods and deposited onto a specific substrate. This way the mechanical properties of the material could be obtained by the utilization of various techniques, such as Raman spectroscopy or atomic force microscopy, as reported earlier in this review. It is very important, however, to study the per-
formance of the material in real-life applications such as in polymer nanocomposites. The simplest way to observe the effect of graphene on a small scale nanocomposite, is by depositing the flake(s) on a polymeric substrate and then coating it/them with another layer of polymer (most commonly by spin coating). This way a model composite is formed, mimicking a structure that can be found in bulk nanocomposites and simultaneously enabling an in-depth study on the effect of graphene by simplifying some of the parameters that affect the bulk nanocomposites significantly (processing parameters, orientation, etc.). The majority of studies on model nanocomposites involve mechanically-exfoliated graphene. The use of large area CVD graphene can however enable the scale up of the production of similar “sandwich-like” polymer/graphene/polymer structures, that can take advantage of the exceptional properties of mono- or few-layer material.

In the consideration of the mechanics of fibre reinforcement, the behaviour of continuous fibres is analysed first, followed by the mechanics of reinforcement by short fibres [213]. In the following sections, it will therefore be demonstrated how model nanocomposites containing either continuous CVD material or short graphene flakes behave, in order to obtain information not only on the reinforcement but also on the structural characteristics and interaction of the graphene with the polymer layers and under strain.

6.1. Monolayer graphene

6.1.1. Continuous CVD material

Vlassiouk et al. [214] prepared macro-scale polymer/graphene laminates and fibres using large sheets of CVD graphene and thin PMMA film (Fig. 10a). The modulus of the laminates was double compared to that of the PMMA matrix with only 0.13 vol% of graphene, while the strength was increased by 25%. The 2D and G band shifts were monitored as a function of strain and the shift of the bands were in the region of $\sim 25 \text{ cm}^{-1}/\%$ and $\sim 10 \text{ cm}^{-1}/\%$, respectively (Fig. 10b and c). The maximum strain before break was around 5%, while the characteristic linear response of the band shift was observed up to 1% strain. The effective modulus of CVD graphene used in the composites can be calculated by using the simple rule of mixtures (ROM) if the assumption that there is good stress transfer between the polymer layers and the graphene monolayer, is made. The volume fraction in this kind of structures can be obtained from the ratio of the graphene thickness (0.34 nm) to that of the nano-sandwich. This work is an excellent example of how the unique properties of graphene can be exploited, since the effective modulus ($E_{\text{eff}}$) of graphene was found equal to 1.2 ± 0.5 TPa showing perfect stress transfer and additional stiffness effects induced in the polymer, by interaction with graphene and by the orientation of the macro-

![Fig. 10.](image)

(a) Scheme of laminates and scrolls used, (b) downshift of the G and 2D bands and (c) Raman spectra for a graphene/PMMA laminate sample. Reprinted (adapted) with permission from [214]. Copyright 2015 American Chemical Society.
molecular chains at the interface. It should be stated though, that the $E_{\text{eff}}$ of graphene is not in accordance with the observed downshift of the 2D band during the bending procedure, since a modulus of 1 TPa is associated with a downshift of around $-60 \text{ cm}^{-1}/\%$ [190]. The strength of graphene was also calculated after applying the ROM for the tensile strength values and it was equal to $11 \pm 6.7 \text{ GPa}$, which is significantly lower compared to the 130 GPa, reported by Hone and coworkers for mechanically-exfoliated graphene [5]. This behaviour can be rationalized from the polycrystalline nature of graphene with grain boundaries between different domains which is known to reduce the strength of the material. Moreover, large scale CVD graphene can have a significant number of defects at random locations that can reduce the strength of the material. Additionally, the transfer procedure that is needed for sandwich structures can also introduce ruptures and tears in graphene that can affect the strength but not the modulus of graphene.

Strano and coworkers recently published work [215] very similar to that of Vlassiouk et al. [214] on the use of CVD graphene for the bulk production of laminates and scrolls of polycarbonate (PC) composites. The number of graphene layers ranged from 8 to 320 and the respective volume fractions were from 0.003 to 0.185%. The authors claimed that the graphene layers remained intact by observing the translucent area containing graphene. The effective modulus of graphene in the laminates calculated by the rule of mixtures is equal to 360 GPa, which is significantly lower than the commonly-accepted value of 1 TPa, possibly because of rippling or breaking of graphene during the preparation of laminates, which could not be

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**Fig. 11.** (a) Stress-strain response for the PEMA bilayer and PEMA/graphene nano-sandwiches at 80 °C and (b) shear stress and strain variation at a strain of 0.18% for a 68 nm thick nano-sandwich using shear-lag analysis. Reprinted from [216]. Copyright 2014, with permission from Elsevier.

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**Fig. 12.** (a) Strain mapping of a coated and uncoated monolayer graphene at different strain levels, (b) strain mapping of coated monolayer graphene in the relaxed state and then reloaded to 0.8% and 0.6% strain. Reprinted (adapted) with permission from [219]. Copyright 2011 American Chemical Society.
observed on the surface of the laminates. Ideally, the authors should have performed Raman experiments combined with a bending procedure, in order to obtain reliable information on the effective modulus of graphene and the structural integrity of the flakes. The spiral fibres also exhibit higher values of storage modulus than the PC matrix but lower stiffness than their laminate counterparts. Their effective modulus was equal to 500 GPa, higher than the one observed on the laminates, as a result of the reduction of the in-plane ripples.

In an earlier report, Li and McKenna [216] prepared similar “sandwich” structures by incorporating sheets of CVD graphene between rubbery poly(ethyl methacrylate) (PEMA) layers. The nano-bubble inflation method, developed by the same group [217,218] was applied for the study of the stress-strain responses of the nano-sandwich and it was found that the height of the graphene-reinforced nano-bubbles was lower than ones of the neat polymer, as a result of the stiffening effect of graphene. The biaxial strain as a function of pressure was obtained from the height profiles and the stress-strain responses were plotted (Fig. 11a). The greater stiffness of the graphene structures is obvious from the slope of the linear fits and by applying the simple rule of mixtures, the biaxial modulus of the CVD graphene was calculated equal to 511 GPa, again as a result of wrinkles and defects in graphene that lower its modulus below the accepted value of around 1 TPa. Shear lag analysis was also used with the experimental data and when the strain reached 0.18% the interfacial shear stress reached a critical value and the slippage or failure occurred (Fig. 11b). The interfacial shear strength at this point was calculated equal to be 0.48 MPa, which is lower than the values reported by Gong et al. [178] for a graphene/PMMA system, who found that slippage in their system occurred at 0.4% strain.

6.1.2. Short flakes

The majority of the fundamental research upon the mechanical properties of model graphene-based nanocomposites involves short graphene flakes, prepared by mechanical exfoliation and sandwiched between two polymer layers. In order to map the strain distribution in a graphene monolayer nanocomposite, Young et al. [219] placed monolayer graphene between two layers of polymer and it was found that for strains lower than 0.6% the distribution of strain is uniform and mapping can be performed precisely (Fig. 12a). The formation of possible cracks in the polymer coating layers at strains higher than 0.6%, leads to lowering of interfacial shear stress to around 0.25 MPa, which is an indication of poor adhesion between the components of the system. The sample was mapped afterwards in a relaxed state as it can be seen in Fig. 12b and the strain fell to around 0.1% but it was not as homogeneous as it was before deformation (Fig. 12a). When the sample underwent reloading at 0.8% strain, the distribution of strain was quite non-uniform; there were three vertical regions of high strain across the monolayer and other areas were subjected to lower levels of strain. The same picture was formed when the sample was further reloaded to 0.6% strain. Therefore, it can be understood that loading a monolayer graphene to 0.8% strain can cause damage to the interface between graphene and the polymer as a result of polymer fragmentation or cracking of the polymer coating. Other interesting conclusions that came out from this work are that for low strains, both coated and uncoated graphene exhibit similar strain distribution, while the unloading procedure leads to residual strain to the polymer beam, of the order of 0.15%, due to creep phenomena.

The strain mapping enables the study of the stress transfer from the polymer to graphene, and in similar work from Gong et al. [178], exfoliated monolayer graphene was placed between two PMMA layers and the authors studied the stress induced shifts of the G’ (2D) band. The downshift of the band was observed up to 0.4% strain and then the sample remained at the specific strain for mapping. Afterwards it was loaded up to 0.7% strain and then the specimen was unloaded. The band shifts became irregular after mapping, due to relaxation phenomena (Fig. 13). Moreover, it can be seen that the unloading procedure produced a line with a slope much higher than the one of the loading procedure (around –60 cm⁻¹/%), while the posi-

Fig. 13. Shift of the 2D band position as a function of strain in a monolayer graphene nanocomposite. Reprinted (adapted) with permission from [178]. Copyright 2010 American Chemical Society.
tion of the 2D band was found at higher wavenumber than the initial measurement, indicating slippage of the graphene in the composite during loading, which was subjected to in-plane tensile deformation on unloading.

The strain was found to build up from the flake edges towards the middle at low strain ($e_m = 0.4\%$) indicating good bonding between graphene and matrix, while at higher strains ($e_m = 0.6\%$) the interface between polymer and graphene fails at some point and stress transfer takes place through interfacial friction. The strain distribution at 0.4% strain was analysed using the shear-lag theory\cite{220,221}, where it is assumed that there is elastic stress transfer from the matrix to the reinforcement through shear stress at the interface. For a given matrix strain $e_m$, the variation of strain in the flake $e_f$, with position $x$, across the monolayer, the shear-lag theory takes the form:

$$e_f = e_m \left[1 - \frac{\cosh (n s x)}{\cosh (n s)}\right]$$

where $n = \sqrt{\frac{G_m}{T}}$ and $E_m$ is the Young's modulus of the flake, $G_m$ is the shear modulus of the matrix, $l$ is the length of graphene in the $x$ direction, $t$ is the thickness of the flake, $T$ is the thickness of the resin and $s$ is the aspect ratio of graphene. The shear-lag fitting parameter $n$ can be taken as an indication of the stress transfer efficiency between the flake and the matrix and depends both on the interactions and the morphology of the flake. The most efficient reinforcement can be obtained when the product of $ns$ is high; therefore, high aspect ratio is always desirable for the reinforcement of the composite. The good fit of the experimental data using the shear-lag theory is an indication that the interface between polymer and graphene remained intact at this level of strain\cite{178}.

The critical length of reinforcement ($l_c$), which is defined as $2 \times$ the distance over which the strain rises from the edges of the platelet to the plateau level, can be also obtained from Fig. 14a. It can be seen that the strain rises to about 90% of the plateau over about 1.5 µm from the edge of the flake, making the critical length of reinforcement around 3 µm and according to the general assumption that the efficient reinforcement needs flakes or fibres with lengths 8–10 times higher than the $l_c$, flakes of 25–30 µm are needed for efficient reinforcement in composites. Similar results were reported from Anagnostopoulos et al.\cite{222} who studied the distribution of stress along a supported monolayer graphene flake in detail by Raman line mapping near the edges of the flake. The authors found out that the preparation method and doping of the flakes can affect the stress transfer mechanism at a distance of 2 µm away from the edges. Therefore, the classic shear-lag theory cannot be applied for the axial stress and interfacial shear stress distributions. Efficient load transfer can take place at around 4 µm from the edge of the flake; therefore they suggested flakes with a size greater than 8 µm are needed for efficient reinforcement.

In a very interesting recent study from Wang et al.\cite{223}, the authors evaluated the effect of graphene functionalization (using a $O_3/H_2O$ gaseous mixture) on the interfacial adhesion between a graphene membrane and PMMA. Functionalization of graphene can induce structural defects that are known to reduce the modulus of graphene but the process can improve the interfacial adhesion by the formation of hydrogen bonds, causing a stiffening and strengthening of the interface. Therefore, there is a fine balance between the degree of functionalization and the ability to achieve better interfacial adhesion. The strain distribution of monolayer, un-functionalized graphene was mapped and fitted successfully with the shear-lag model, while interfacial sliding was observed at 0.7% strain (Fig. 14a). The use of the gaseous mixture successfully functionalized the graphene and the membrane formed hydrogen bonds with the carbonyl groups of PMMA. This treated graphene had as a result a better stress transfer performance, as the slope $d e_f/dx$ was higher than that of the pristine graphene and the
The shear-lag fitting parameter was also significantly higher, indicating superior stress transfer efficiency (Fig. 14b). The interfacial shear strength was also calculated to be 4 times higher than that of un-functionalized material.

Polyzos et al. [224] successfully studied the behaviour of suspended graphene under uniaxial loading, obtaining in this way information about the intrinsic properties of graphene without the effect of the substrate. The sample preparation method involved depositing the monolayer graphene flake on a PMMA beam, spin-coating the flake with another layer of PMMA and then suspending the central part of the flake by removing a specific section of PMMA by e-beam lithography. Uniaxial strain was applied up to 0.8% and a clear splitting of the G band into two components \(G^+/G^0\) was observed, while the slopes of the downshift of the G band was \(\frac{\partial \omega_G}{\partial \varepsilon} = -19 \pm 1 \text{ cm}^{-1}/\%\) and \(\frac{\partial \omega_{G^0}}{\partial \varepsilon} = -37 \pm 2 \text{ cm}^{-1}/\%\), in accordance with the results of Mohiuddin et al. [169] who deformed suspended graphene flakes in air. The same picture was found for the 2D band, where the splitting was observed once again and very large shifts, of the order of \(-84 \text{ cm}^{-1}/\%\) and \(-94 \text{ cm}^{-1}/\%\) were observed for the 2D1 and 2D2 peaks, respectively. The results showed that the stress is transferred to the suspended part of the flake over large distances (>2 \(\mu\)m) and the measured interfacial shear stress was 0.75 MPa.

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As can be realized, in different investigations, the authors have monitored the strain and the respective shifts of different characteristic G or 2D Raman bands. So the question regarding which band is more suitable to be monitored in such studies comes naturally. In an report from del Corro et al. [225] the authors suggest that the shifts of G and 2D modes might be biased under uniaxial strain, due to the effects of charge-transfer doping. For this reason, they suggested that the 2D’ band is the most appropriate for strain sensing of monolayer graphene, since the splitting, complexity and the doping effects, affect the detailed monitoring of the \(G^0\), \(G^+\) and 2D bands. The downshift observed in various sets of monolayer graphene samples deposited in either SU8, PMMA and PC both covered or uncovered with PMMA, was in the range of \(-21.7 \pm 0.6 \text{ cm}^{-1}/\%\), a value very close to \(-21 \text{ cm}^{-1}/\%\) that was predicted from Narula and Reich [226] by ab initio calculations.

### 6.2. Few layer graphene

Apart from the lateral size of the reinforcement, several other parameters must be taken into account for the evaluation of the ability of a graphene flake to be able to enhance the properties of a matrix. In terms of “model” nanocomposites, Gong et al. [190] evaluated some of these parameters, such as the number of layers that can effectively reinforce a polymer. The authors used two of the most useful Raman spectroscopy functions in graphene studies; strain mapping and strain-induced band shifts in coated and uncoated graphene deposited on a polymer beam. It was found that coating does not affect the rate of band shift per unit of strain for monolayer graphene (which was \(-59 \text{ cm}^{-1}/\%\) at both situations) (Fig. 15a). For two-layer graphene, the shift rate of the uncoated sample \((-31 \text{ cm}^{-1}/\%)\) was lower than the coated one \((-53 \text{ cm}^{-1}/\%)\), indicating poorer stress transfer efficiency in the “model” composites. This can be interpreted as the polymer-graphene interactions being strong, while the stress transfer within the flakes is relatively poor. The deterioration of the stress transfer was also observed from studying a single flake with different mono-, bi-, tri- and many-layer regions, where the rates of band shift per unit of...
strain decrease with an increasing number of layers (Fig. 15b). Moreover, the band shift per unit strain is analogous to the effective modulus of the flakes, therefore it can be understood that bilayer graphene exhibits identical reinforcement efficiency with monolayer, while the efficiency of tri-layer graphene drops by 15%. In fact, the reinforcing efficiency of graphene falls to less than half when the number of layers is higher than 7. Also, according to the authors [190], the stress build-up is homogeneous for flakes with sizes larger than 10 μm.

The number of graphene layers used for the preparation of a polymer composite plays a major role on the efficient reinforcement, since stress transfer takes place from the matrix to the outer layers and is in turn transferred to the inner layers by shear. The stacking of the layers can affect not only the mechanical properties but the electronic and optical characteristics. AB Bernal stacking [227] is the most common arrangement in bilayer graphene and this is the main reason behind the differences of the electronic properties of mono- and bilayer material. Frank et al. [85] initially studied monolayer and Bernal-stacked bilayer flakes under uniaxial deformation and as expected the interfacial failure was observed at lower strain levels for the bilayer graphene. Moreover, the bilayer composite is susceptible to nonuniform strain, which induces an alteration of the bilayer inversion symmetry. Gong et al. [84] extended the study of Frank et al. [85] towards the deformation of few-layer graphene in nanocomposites and the observation of the deterioration of the reinforcement with increasing layer number. For monolayer and bilayer graphene 2D band broadening is observed, while band narrowing is observed for more than two layers. The irregular shape of the 2D band of graphene with three or more layers under zero strain is transformed into a symmetrical shape above ≈ 0.4% strain and during the unloading, it reverts to an asymmetric shape. This is an indication of a reversible loss of Bernal AB stacking during deformation, which leads to the reduction of the effective Young’s modulus of the material. This has as a result of the formation of a basal-plane stacking fault and the elastic strain energy released during the unloading procedure was calculated to be in the order of 0.2 meV/atom. An example of the loss of Bernal stacking in tri-layer graphene can be seen in Fig. 16. When the matrix is deformed the applied stress is transferred to the outer two layers, which become elongated in the tensile direction and narrower in the transverse direction due to Poisson contraction. The stress can be only transferred to the middle layer by the outer layers and if the outer layers are deformed, the inner layer will remain un-deformed and the Bernal stacking will be lost (Fig. 16b).

![Fig. 16. Loss of Bernal stacking of trilayer graphene during affine deformation of a nanocomposite: (a) undeformed structure, (b) deformed structure. Reprinted (adapted) with permission from [84]. Copyright 2013 American Chemical Society.](image)

![Fig. 17. Illustration of the (a) single solvent blending and (b) co-solvent blending method for the preparation of aqueous reduced graphene/thermoplastic polyurethane nanocomposites. Reprinted from [241]. Copyright 2013, with permission from Elsevier.](image)
7. Bulk nanocomposites

The use of a variety of graphene-based materials for the production of bulk nanocomposites is already widespread in academia. The number of reports on "graphene-based composites" has been increasing exponentially since graphene was first isolated in 2004 and there are already several commercial applications implementing graphene materials for the production of high quality, multifunctional composites. A number of reviews have already dealt with the production and properties of graphene-based composites [6,22,228–239] and for this reason we will briefly refer to the general preparation of such materials and focus mainly on the mechanics of deformation.

7.1. Preparation

The most important aim during the manufacturing of graphene/polymer nanocomposites is to ensure that graphene will disperse adequately within the matrix. A homogeneous dispersion will give the best mechanical reinforcement of the matrix. Moreover, the nature of the interface between the graphene and the matrix along with the aspect ratio of the filler are key aspects for the design of polymer-based nanocomposites. A number of preparation strategies have been presented in literature, and the most important ones (solution compounding, melt blending, in situ polymerization and layer by layer assembly) will be discussed next.

7.1.1. Solution compounding

The solution compounding method involves the mixing of a graphene-based suspension with a polymer that is either already in a solution or will be mixed with the graphene suspension (providing that it is compatible with the solvent) by simple or shear mixing or ultrasonication. This suspension can be cast into a mould and then the solvent is removed (which, however, may cause re-aggregation of the filler). Alternatively, the suspension can be precipitated using a non-solvent for the polymer, activating encapsulation of the filler within the polymer molecules during precipitation. In general, solution blending provides adequate dispersion of the flakes and it is quite versatile, since a number of different solvents can be used to dissolve the matrix and disperse the filler. Moreover, it is a facile and fast procedure and for this reason it has been exploited widely [240–272]. This strategy is not free of drawbacks, however. Some of the problems involve the use of toxic solvents, the total elimination of solvents in the final product and the possible re-aggregation of the filler during one of the preparation steps.

Liao et al. [241] produced aqueous-reduced graphene (ARG)/thermoplastic polyurethane (TPU) composites by a solution blending method. The major disadvantage of aqueous reduction of graphene is that when the graphene solution is dispersed in the polymer, the removal of water leads to restacking and aggregation phenomena. For this reason, the authors introduced a co-solvent process, by adding an organic solvent (dimethylformamide-DMF) before the removal of water took place from the aqueous reduction mixture (Fig. 17). Initially, 90% of the water was removed from the ARG suspension in order to avoid aggregation, then DMF was added for the formation of a ARG/H₂O/DMF solution and the polymer was subsequently added to...
this solution. The results showed that compared to the single solvent blending method, the modulus of the co-solvent blended composites was almost double, while compared to the neat TPU it was almost 6 times higher at a filler loading of 3 wt% (where the term “loading”, refers to the filler content), as a result of the better dispersion of the fillers in the matrix.

7.1.2. In situ polymerization

During in situ polymerization, the graphene flakes are mixed initially with monomers or pre-polymers and the polymerization procedure that is performed afterwards leads to the production of composites with good dispersion and strong interac-
tions between the matrix and the flakes [273–288]. The procedure allows the grafting of the filler on the polymer (with or without functionalization) for the enhancement of compatibility between the components of the system. Some difficulties are associated with the increase of viscosity during the polymerization process, that limits the loading fraction and the processing of the composites [289]. In an example that highlights the advantages of this specific method, Wang et al. [278] prepared graphene oxide/polyimide (PI/GO) composites by in situ polymerization. The authors functionalized GO with amine (–NH₂) (ODA-GO) groups in order to promote the dispersion of the flakes and took advantage of the functional groups of GO for the grafting of poly(amic acid) at the reactive sites of the GO nanosheets (Fig. 18). Moreover, the functionalization route enabled the formation of strong interfaces between the filler and the matrix, facilitated load transfer and improved the modulus and tensile strength impressively at a relatively small filler loading (3 wt%).

The oxygen-containing groups of graphene oxide, provide enough active sites to form bonds with the matrix or a secondary filler that can enhance the ultimate properties of the composites. Moreover, it has been shown that GO can be thermally reduced during the polymerization procedure [273], while common catalysts such as TiO₂/SiO₂ nanoparticles can grow on the surface of GO and promote the exfoliation of the flakes during in situ polymerization [290].

In a series of papers from Bielawski and coworkers, GO has been proved to function in two distinct roles during the polymerization procedure [291–294]. It can initially catalyze the dehydrative polymerization, while the residual carbon from the GO catalyst undergoes a dehydrogenation during the reaction and ultimately serves as a graphene-like additive in the composite. The importance of this research lies in the fact that this approach can allow a single-step formation of composites with high molecular weight and enhanced properties, by using just two reactants: a monomer and the GO.

7.1.3. Melt mixing

Melt mixing is the procedure followed most widely in industry for the production of thermoplastic nanocomposites since it is fast, inexpensive and relatively simple. It involves melting the polymer at elevated temperatures and mixing the graphene flakes (in a powder form) using a single-, twin-, triple- or even quad-screw extruder. Several graphene-based nanocomposites have been prepared with this technique [295–309]. The results in general show that melt mixing produces composites with an adequate degree of dispersion, while care should be taken during the preparation procedure on the mixing temperatures, since working at elevated temperatures can cause a degradation of the polymer. Moreover, the high shear forces that are sometimes required for the efficient mixing of the polymer with the flakes may even cause a buckling or breakage of the graphene sheets. In general, even though melt mixing usually leads to a poorer dispersion than in situ polymerization or solution blending [302,310], the preparation of composite materials with adequate properties and the potential of this process for scale-up are enough in order to be adopted widely for the preparation of graphene-based nanocomposites.

Modifications of the melt mixing procedure aim towards the improvement of the dispersion and the subsequent enhancement of the properties of the composite. Li et al. [311] used force assembly, a type of multilayer coextrusion (Fig. 19), which was originally developed by Baer and coworkers for the combination of immiscible polymer blends into unique polymer structures [312,313]. This process induced orientation of the graphene nanoplatelets introduced into poly(methyl methacrylate)/poly(styrene) (PMMA/PS) and PMMA/PMMA multilayer films. The planar orientation of the filler led to a higher degree of

![Fig. 19. The multilayer coextrusion process followed by Li et al. for the production of multilayered polymer nanocomposites with alternating layers of unfilled polymer and polymer containing oriented graphene. Reprinted from [311]. Copyright 2014, with permission from Elsevier.](image-url)
reinforcement in the composites, since at 2 wt% graphene loading in a PMMA/PMMA system, a significant improvement was reported for the modulus. This work is an example of the effect of the orientation of the fillers in composites, along with the modification of the traditional and simple preparation strategies towards the improvement of the structure and homogeneity of the final material.

7.1.4. Layer by layer (LbL) assembly

Layer by layer (LbL) assembly is a versatile technique that has been explored continuously over the past few years for the production of graphene-based composites. In LbL assembly various nanomaterials with desired nano-architectures can be combined for the production of multilayer thin films of specific thickness or hierarchical nanostructures by alternating anionic and cationic phases on a substrate. By adjusting the deposition sequence, novel functional materials can be prepared for a wide variety of applications, including Li-ion batteries, membranes, anodes, field-effect transistors and supercapacitors. The parameters that play a major role in the use of the LbL assembly include temperature, pH, ionic strength and the actual polyelectrolyte along with the factors that can affect the interactions; hydrogen and covalent bonding, electrostatic, charge-transfer and coordination chemistry interactions. Graphene has been proven to be an excellent building block in this context, therefore graphene-based 2D or 3D multilayer films and nanostructures are already being explored. Moreover, GO with the various hydroxyl and epoxy groups on the basal plane and carboxyl and carbonyl group on the edges, can increase the electrostatic attractive interactions and hydrogen bonding during LbL assembly. The current status of the specific technique has been summarized in a recent review by Xiao et al. [314].

Zhao et al. [315] prepared (PVA/GO)ₙ multilayer films with a bilayer thickness of 3 nm by LbL assembly and found that the modulus of the composite was doubled, compared to the pure PVA film. Additionally, during the nanoindentation measurements, the penetration depth of the multilayer film decreased significantly, as a result of the enhanced hardness the nanometer-level assemblies and the orientation of the GO.

7.2. Composite micromechanics

Over the years, a number of different theories have been proposed for the study of the micromechanics of composite materials with an ultimate goal of being able to predict the effective behaviour of a heterogeneous material within a matrix. There are generally two schools of thought in considering the mechanical properties of polymer-based nanocomposites. Some people assume their mechanics to be similar to those of composites with macroscopic reinforcements, such as carbon and glass fibres [22]. Another group of researchers [316,317] have taken an opposing viewpoint and have suggested polymer nanocomposites are actually quasi-homogeneous molecular blends, that ought to be regarded as molecular composites or self-reinforced composites. In this case they have suggested that the classical micromechanical models developed for normal composites cannot be applied and that the properties are controlled by interactions on the molecular scale between the nanoparticles and the polymer matrix [316]. This approach has received considerable support particularly from groups working upon carbon nanotube-based composites. There are clearly issues such as crystal nucleation and molecular confinement that cannot be explained through micromechanics. Nevertheless, in this present review we demonstrate that there is overwhelming evidence that the mechanical properties of graphene-reinforced polymers can be modeled broadly using classical composite micromechanics, particularly at low levels of graphene loading. We will show, however, to what extent this approach can be employed and when other methods may have to be used.

In micromechanics the individual materials are treated as continua via continuum mechanics and the ultimate properties of the composite material are strongly affected by their individual properties and arrangement [318]. Even though some micromechanical theories had success in the prediction of the mechanical properties of composite samples, the randomness of each individual system and the properties of all the components of the system make this task very difficult. Moreover, the structural and geometrical characteristics of the filler, the possible formation of an interphase along with the orientation or the distribution in the matrix, play a major role that need to be reflected in these theories. The usefulness of the specific theories lies in assisting the design of the composite materials, along with the reinforcement geometries.

7.2.1. Analytical methods

One of the simplest relationships that has been developed to describe the reinforcement achieved from a high-modulus filler in a low-modulus matrix, is the so-called “rule of mixtures", in which the modulus of the composite is given by [213]:

$$E_c = E_f V_f + E_m (1 - V_f)$$  \hspace{1cm} (7.1)

where $E_c$, $E_m$ are the modulus of the filler and the modulus of the matrix and $V_f$ and $V_m$ are the volume fractions of the filler and the matrix respectively. The use of the rule of mixtures involves making assumptions regarding the uniform distribution and the perfect bonding of the filler in the matrix, while the matrix should also be free of voids (although if the void content is known it can be taken into account by another term in the equation). Despite its simplicity, this equation has been found to predict well the modulus of the composites, especially at low loadings but it should always be considered as an approximation, since it does not take into account important factors such as the Poisson’s ratio (amongst others). At higher filler contents, the unavoidable aggregation of the filler is not taken into account from this linear equation and in most cases the theory is not applicable at high loadings.
As mentioned earlier, the orientation and size of the filler plays a major role in the reinforcement, and for this reason a modified rule of mixtures has been proposed for short reinforcement systems:

\[ E_c = E_{eff}V_f \eta_o \eta_l + E_m(1 - V_f) \]  

(7.2)

where \( E_{eff} \) is the effective modulus of the filler, \( \eta_o \) is the Krenchel orientation factor which depends on the average orientation of the filler with respect to the applied stress, while \( \eta_l \) is the length distribution factor and takes values between 0 and 1, depending from the poor stress transfer arising from poor interfaces and/or short flakes. The length distribution factor for short flakes can be given by:

\[ \eta_l = 1 - \frac{\tanh \left( \frac{s}{n} \right)}{\frac{s}{n}} \]  

(7.3)

where \( s \) is the aspect ratio and \( n = \sqrt{\frac{E_m}{E_f}} \). The length distribution factor also assumes that the matrix and the filler remain elastic during deformation, interfacial bonding is perfect, the shear stress at the end of the filler is maximum and falls to zero after half the “critical length”. Additionally, the tensile stress at the filler ends is zero and rises to maximum after half the “critical length” [178]. For a continuous fibre, the length distribution factor is equal to 1.

In two recent reports from our group [319,320], the Krenchel factor for 3D randomly oriented nanoplatelets was calculated and quantitative determination of the spatial orientation of graphene in a nanocomposite was undertaken. Polarized Raman spectroscopy can be used for the quantification of the level of spatial orientation in a graphene based nanocomposite. The spatial orientation of the fillers is of utmost importance in nanocomposites, since the reinforcement is the highest for graphene aligned in the direction of strain. The local orientation of graphene can be defined by its surface normal, which
is the z direction of graphene in the x, y plane, observed in Fig. 20a. The orientation distribution function (ODF) of the surface normal can be written as \( f_o(\theta, \varphi, \xi) \). By using the VV laser polarization, the Raman scattering intensity can be expressed in terms of the polarization angle \( \Phi \), relative to the sample as:

\[
I_{\text{sample}}(\Phi) = I_0 \left\{ \frac{8}{15} + \langle P_2(\cos \theta) \rangle \left( \frac{-16}{21} + \frac{8}{7} \cos^2 \Phi \right) + \langle P_4(\cos \theta) \rangle \left( \frac{8}{35} - \frac{8}{7} \cos^2 \Phi + \cos^4 \Phi \right) \right\}
\]

where \( I_0 \) is the amplitude and it is also assumed that there is a homogeneous distribution of the surface normals around the Z-axis, \( P_i(\cos \theta) \) in general is the Legendre polynomial of the i-th degree and \( \langle P_i(\cos \theta) \rangle \) is the average value. In this case, \( \langle P_2(\cos \theta) \rangle \) is Hermans orientation factor, \( S \) [321]. Generally, the higher the values of \( \langle P_2(\cos \theta) \rangle \) and \( \langle P_4(\cos \theta) \rangle \), the higher the degree of orientation of the flakes in the composite. Therefore, fitting one's experimental data to this equation, a set of \( \langle P_2(\cos \theta) \rangle \) and \( \langle P_4(\cos \theta) \rangle \) values can be obtained to quantify the spatial orientation of graphene [320]. Based on these values, the ODF can be obtained as:

\[
f_o(\theta) = A \exp[-(\lambda_2 P_2(\cos \theta) + \lambda_4 P_4(\cos \theta))]
\]

where the coefficients \( A, \lambda_2 \) and \( \lambda_4 \) can be solved numerically, as indicated in [320,322]. This then leads to [320]:

\[
\eta_o = \frac{8}{15} + \frac{8}{21} \langle P_2(\cos \theta) \rangle + \frac{3}{35} \langle P_4(\cos \theta) \rangle
\]

which shows that the orientation factor is dependent only on \( \langle P_2(\cos \theta) \rangle \) and \( \langle P_4(\cos \theta) \rangle \). Hence it can be calculated directly from the experimental measurements of the angular dependence of the polarized Raman scattering intensities. Therefore, fitting Eq. (7.4) to the experimental data can give the two parameters that can be used directly in Eq. (7.6) to determine the Krenchel orientation factor. It should be realized that for a perfectly-aligned platelet-based composite \( \langle P_2(\cos \theta) \rangle = \langle P_4(\cos \theta) \rangle = 1 \) while for 3D randomly oriented materials \( \langle P_2(\cos \theta) \rangle = \langle P_4(\cos \theta) \rangle = 0 \). Therefore, the Krenchel factor for an oriented material is equal to 1, while for a material reinforced with randomly aligned nanoplatelets, it is equal to 8/15.

Hence, the random orientation of the plate-like fillers should cause a reduction of the modulus by less than a factor of two, compared with a fully-aligned material (Fig. 20b). Moreover, from this study, it was realized that the reinforcing efficiency of nanoplatelets, is much higher than fibre- or nanotube-based materials (when both have random orientation), since according to the original work of Krenchel [323], since for these materials random orientation reduces the modulus by a factor of five (\( \eta_o = 1/5 \)).

The effective modulus of the flakes can be also calculated from the slope of the \( E_c \) versus filler loading curve. In an example of the application of the modified rule of mixtures (MROM), an epoxy resin was reinforced by GO nanoplatelets and the effective modulus of the GO was found to be equal to 90 GPa, while the particle modulus was found to be equal to 169 GPa assuming \( \eta_l = 1 \) [324]. This value can be compared with the accepted modulus value of 200–250 GPa [4,154] and the discrepancy may be due the presence of short flakes, so that \( \eta_l < 1 \). Moreover, it was confirmed once again that the reinforcement of the modulus from GO saturates at significantly smaller filler loadings than graphene nanoplatelets and this time a plateau was found after a loading of 1 wt% (Fig. 20c).

Fig. 21. (a) Experimental values and fitting with the Halpin-Tsai theory for an epoxy/GNP set of samples [328], Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. (b) Modulus versus loading for the PMMA/GO and PMMA/RG-O samples. The lines represent the values from the Mori-Tanaka equation using different values for the modulus of the flakes and their aspect ratio. Reprinted from [274]. Copyright 2011, with permission from Elsevier.
7.2.2. Semi-empirical methods

Since the reinforcing efficiency is strongly affected by the geometrical characteristics of the filler, the latter have been incorporated in several semi-empirical equations, such as the ones from Halpin and Tsai [325], which have been used successfully in a variety of composite systems. Moreover, the Halpin-Tsai equations can take into account the orientation of the filler towards either the longitudinal (L) or the transverse (T) directions and take the form:

\[
\frac{E_L}{E_m} = \frac{1 + \frac{\eta_L}{1 - \eta_L} V_f}{1 - \frac{\eta_L}{1 - \eta_L} V_f}, \quad \frac{E_T}{E_m} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f}
\]

where the parameter \(\eta\) is given by:

\[
\eta_L = \frac{E_f / E_m - 1}{(E / E_m) + \frac{\zeta}{\varepsilon}}, \quad \eta_T = \frac{E_f / E_m - 1}{(E / E_m) + 2}
\]

\(E_i\) is the tensile modulus of the filler and \(\zeta\) is a shape fitting parameter, which takes into consideration the geometry of the reinforcing fibres along with the packing arrangement. Several reports have adapted \(\eta\) for the particular characteristics of their filler and especially on their aspect ratio (s) but in general for the case of nanoplatelets \(\zeta = 2/3\) [326], while for the case of fibres \(\zeta = 2s\) [327]. For two-dimensional random orientation of the fillers the composite tensile modulus is given by the equation: \(E_C = \frac{3}{8} E_L + \frac{5}{8} E_T\), while for three-dimensional random orientation of the fillers it is given by: \(E_C = \frac{1}{5} E_L + \frac{4}{5} E_T\). In a good example of the application of the Halpin-Tsai equations, King et al. [328] confirmed that the 2D orientation of the fillers that was intentionally caused by their preparation method (shear mixing) and observed with optical methods, can be also confirmed as well from fitting the tensile modulus data with the Halpin-Tsai theory (Fig. 21a).

The Mori-Tanaka model has also been used for the evaluation of the tensile characteristics of composites, since it describes the internal stress in a material containing solid inclusions, under transformation strain [329]. The Poisson ratio and the moduli of the matrix and the fillers along with the aspect ratio of the fillers, are used for the evaluation of the transverse modulus of the composite materials. The Mori-Tanaka model was modified by Tandon and Weng to describe the modulus of composites reinforced with randomly oriented, mono-dispersed ellipsoids [330]:

\[
E_C = \frac{E_m}{1 + V_f(-2v_m A_3 + (1 - v_m) A_4 + (1 - v_m) A_5 A)/2A}
\]

\[
E_C = \frac{E_m}{A + V_f(A_1 + 2v_m A_2)}
\]

where \(E_C\) is the transverse (Eq. (7.9)) and the longitudinal (Eq. (7.10)) composite modulus respectively, \(V_f\) is the loading of the filler and \(v_m\) is the in-plane Poisson’s ratio of the matrix. The parameters \(A\) and \(A_i\) are based on the volume fraction and the modulus of the filler, the modulus of the matrix and the Poisson ratio of the fillers and they are components of Eshelby’s tensor [331,332] described in the original equations from Tandon and Weng [333]. In an example of the application of the Tandon and Weng modification of Mori-Tanaka theory, Potts et al. [274] applied the equation to the experimental data obtained from tensile testing poly(methyl methacrylate) (PMMA) reinforced with GO. The results presented in Fig. 21b show that the equation is valid at low loadings (up to 1 wt%) and for a certain aspect ratio of 100. The theory does not however take into account the aggregation phenomena and this is why it fails to predict the modulus at higher loadings.

Fig. 22. (a) Characteristic stress-strain curves for the PU/D-Graphene nanocomposites and (b) Young’s modulus values for the nanocomposites. Reproduced from [334] with permission from The Royal Society of Chemistry.
7.2. Mechanical properties

The presence of the high-modulus graphene in a low modulus matrix can lead to significant reinforcement and for this reason a vast amount of research has been focused on the mechanical properties of graphene nanocomposites. The evaluation of the reinforcement in graphene-based nanocomposites is most commonly performed by the study of the stress-strain curves obtained during tensile testing. Several parameters can affect the mechanical properties of graphene-based nanocomposites including the structure of the graphene, the preparation method, the dispersion of the filler in the matrix, the filler-matrix interactions and the orientation of the filler. The Young’s modulus and tensile strength along with the toughness can show significant increases even with a very small amount of filler. The tensile strength is, however, heavily affected by aggregation of the filler and that is why it is often found that there is a linear increase of the tensile modulus with increasing filler content, while tensile strength saturates at lower filler percentages. Furthermore, graphene oxide is often preferred over few- or many-layer graphene nanoplatelets (even though the modulus of GO is only about 25% of that of monolayer graphene) since the presence of functional groups in GO enables easier coupling interactions between the filler and the matrix.

7.3. Stiffness, strength and toughness

There is a large number of papers in the literature upon the mechanical properties of nanocomposites reinforced with “graphene” and it is not possible to discuss them all in detail and so just a few examples will be described here. In a typical study of the reinforcement of a matrix at low filler loadings, Yang et al. prepared polyurethane composites reinforced with polydopamine-coated reduced graphene oxide sheets (coded D-Graphene in the manuscript) by solution blending [334]. The filler loadings ranged from 0.05 to 0.94 vol%, and the modulus of the composite with the highest filler loading was almost 6 times higher than that of the matrix (Fig. 22). This example is another indication that the modulus of the graphene-based composites presents a significant percentage increase when the modulus of the matrix is low, such as in elastomeric materials [7]. Moreover, it should be noted that the strain at break does not necessarily decrease with the introduction of graphene, even though aggregated fillers are known to act as failure points during the elongation of a composite material [335].

Several investigations have tackled the important issue of the simultaneous enhancement of stiffness, toughness and ductility. There is a number of papers that have reported an increase of the elongation of a composite material as a result of the preparation and functionalization procedure [336–340] that leads to improved dispersion (especially at low filler contents) [341–344] and decreased crosslinking of the matrix [345]. Another interesting strategy is the construction of hidden lengths (dissociation of hydrogen bonds between the PU oligomer which are covalently bonded to graphene nanosheets and polymer chains) and sacrificial bonds (π-π interactions between graphene nanosheets and pyrene derivatives) in the interface between the filler and the matrix such as in the work of Chen and Lu [346].

Yu et al. [257] prepared PVA composites with two sets of graphene-based fillers; reduced GO (rGO) and aryl diazonium salt functionalized graphene (ADS-G). The results showed that rGO gave less reinforcement than the ADS-G. This work shows that functionalized graphene enhances the mechanical properties of a composite better than rGO as a result of improved chemical interactions and the intrinsic mechanical properties of the filler. Moreover, from the results it is clear once again that the enhancement that GO can contribute saturates at a lower content than for graphene.

Besides the information that can be obtained from the engineering stress-strain curves, properties such as the storage or loss modulus from dynamic mechanical analysis (DMA) over a wide temperature range can be evaluated. Similar to the tensile modulus, the storage modulus can improve with the addition of very small amounts of graphene. Zhang et al. incorporated polybenzimidazole-functionalized graphene nanoplatelets (fGnP) into an epoxy matrix [347]. The functionalization of the flakes enabled better dispersion and as a consequence higher reinforcement than for the un-functionalized flakes. The storage modulus versus temperature graph for this set of samples can be seen in Fig. 23, where it is obvious that only 0.5 wt% of fGnP led to an almost 50% increase of the storage modulus.

Fig. 23. DMA curves of fGnP/epoxy composites. Reprinted from [347]. Copyright 2014, with permission from Elsevier.
The fracture toughness is another interesting aspect of the mechanical properties of graphene-reinforced composites that has been studied. Zaman et al. [348] produced epoxy composites with 4,4'-methylene diphenyl disocyanate-functionalized graphene nanoplatelets (GP) and found that at 4 wt% loading, the fracture toughness reached its maximum value at 85% higher than the matrix, while the energy release rate, led to a 200% increment at the highest filler content (5.5 wt%) (Fig. 24).

In an attempt to collate as much information as possible for the mechanical properties of graphene-based nanocomposites that exist in literature, Table 2 has been prepared, where the main mechanical properties of a wide range of nanocomposites have been listed. The improvement of the properties is shown first of all as a percentage increase in the property compared to the matrix. This is how it is often presented in the literature, but it can be misleading since it depends very much upon the properties of the matrix material. For example, if the mechanical properties of the matrix are relatively poor then the improvement from adding the graphene may appear to be relatively good, even though the actual properties of the nanocomposite might be quite modest.

In the analysis of the effect of graphene upon the Young's modulus of the nanocomposites in this present study, the modulus of graphene has been calculated from the literature data using the rule of mixtures (Eq. (7.1)). These calculated values should not be taken as absolute, since parameters such as the Poisson's ratio have not been considered. Where necessary the weight fraction of filler has been converted into volume fraction using an estimated density of the carbonaceous filler of around 2 g/cm³. Given the fact that there is large number of papers concerned with the mechanical properties of graphene-reinforced polymer nanocomposites and since this study can be considered as a continuation of our review on graphene micromechanics published in 2012 [22], the majority of the research that is reviewed corresponds to the time period from 2011 to the present. Table 2 lists the reported mechanical properties of different polymers reinforced with different graphene types from papers published over this time period.

Table 2 is structured initially based on the type of graphene that the authors have used (GNP, GO, rGO) and then categorized based on the polymer matrix that has been used each time. The “GNP” term has been used to collectively include graphene nanoplatelets and nanosheets (GNS) regardless of the thickness of the materials, which unfortunately, sometimes is not provided in the respective works. Once again here, the problem of the standardization and nomenclature of graphene-based materials needs to be addressed. The type of graphene prepared plays a major role on the final properties of the composite material and therefore present and future studies should classify and characterize very carefully the type of graphene under study. In several of the studies listed in Table 2, the authors have prepared “graphene” by the reduction process of graphene oxide, and ended up with a medium or even low quality material containing both intrinsic and extrinsic defects. Moreover, the characterization route that has been followed does not enable the reader to understand clearly if the material obtained is indeed few- or many-layer graphene or partly-reduced graphene oxide and come to solid conclusions about the quality of the flakes, attributes that are critical for the production of high-performing graphene-based nanocomposites.

7.3.2. Assessment of the level of reinforcement

If we examine the results from Table 2 carefully, it can be seen that in terms of the enhancement in mechanical properties upon the addition of graphene, the matrices with the lower modulus (such as elastomers) show higher percentage increases in parameters such as stiffness and strength than rigid matrices. In contrast, it appears to be more difficult to observe similar increased values of stiffness and strength for stiffer materials, such as thermoplastics or thermosetting network polymers. What is more interesting though is that the modulus of graphene \( E_f \) (determined from the rule of mixtures) is actually higher when the matrix is more rigid and the filler loadings are relatively small.

The modulus of the graphene-based fillers is plotted separately for all the GNP-, GO- and rGO-based materials (Fig. 25) listed in Table 2 in a log-log plot as a function of the modulus of the matrix. It can be seen that although there is considerable scatter in the data, for each type of filler the data follow a linear relationship each one with a slope of approximately unity in each case. This behaviour is quite remarkable since the data have been taken from a large number of publications dealing with many different polymeric matrix materials, ranging from soft elastomers to rigid polymers, and a number of different

![Fig. 24.](image-url)
Table 2
Mechanical properties of graphene-based nanocomposites. The optimum loading corresponds to the loading where the increase of the tensile modulus was maximum. When a different property (i.e. tensile strength) shows maximum at a different loading, it will be noted separately.

| Graphene type | Matrix | Preparation method | Optimum loading | Matrix modulus $E_m$ (GPa) | Tensile modulus increase (%) | Graphene modulus $E_f$ (GPa) | Tensile strength increase (%) | Fracture toughness increase % | Ref. |
|--------------|--------|-------------------|-----------------|-----------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|------|
| GNP          | Epoxy  | Three roll mill   | 8 wt%           | 2.8                         | 22                           | 14                           | 24 at 3 wt%                   |                               | [365]|
| GNP          | Epoxy  | Three roll mill   | 1 wt%           | 2.67                        | 8                            | 45                           | 80                            |                               | [366]|
| GNP          | Epoxy  | Three roll mill   | 2 wt%           | 2.5                         | 10                           | 27.5                         |                               |                               | [367]|
| fGNP         | Epoxy  | Three roll mill   | 1 wt%           | 2.4                         | 15.8                         | 106                          | 59 at 0.5 wt%                 |                               | [368]|
| GNP          | Epoxy  | Mechanical mixing  | 5 wt%           | 3.0                         | 27                           | 35                           | 18 at 2.5 wt%                 |                               | [369]|
| GNP          | Epoxy  | Shear mixing      | 6 wt%           | 2.72                        | 23.5                         | 20                           | –54                           |                               | [328]|
| GNP          | Epoxy  | Solution blending | 5 wt%           | 2.7                         | 49                           | 55                           | –36                           |                               | [370]|
| GNP          | Epoxy  | Solution blending | 1 wt%           | 2.9                         | 24                           | 143                          | –72                           | 58                            | [371]|
| GNP          | Epoxy  | Solution blending | 1.18            | 11.5                        | 35.5                         | 11                           |                               |                               | [372]|
| GNP          | Epoxy  | Solution blending | 0.1 wt%         | 2.8                         | 31                           | 1782                         | 42                            | 53                            | [373]|
| GNP          | Epoxy  | Solution blending | 5 wt%           | 2.5                         | 28                           | 30.5                         | 3 at 1 wt%                    |                               | [374]|
| GNP          | CTBN/epoxy | Solution blending | 3 wt%           | 3.75                        | No                           |                              |                               | 109                           | [375]|
| fGNP         | Epoxy  | Solution blending | 1 vol%          | 2.6                         | 24                           | 65                           | –30                           | 188 at 0.25 vol%              | [376]|
| fGNP         | Epoxy  | Solution blending | 2 vol%          | 2.6                         | 37                           | 50                           | –36                           | 135 at 1                      | [248]|
| fGNP         | Epoxy  | Solution blending | 0.75 wt%        | 1.8                         | 61                           | 300.5                        | 59                            |                               | [383]|
| fGNP         | PBS    | Solution blending | 2 wt%           | 0.5                         | 83                           | 37                           | 21                            |                               | [384]|
| fGNP         | PMMA   | Melt mixing       | 20 wt%          | 2.3                         | 74                           | 18                           |                               |                               | [385]|
| fGNP         | PTFE   | Ball mixing/hot   | 3 vol%          | 0.8                         | 223                          | 61                           | 39 at 1 wt%                   |                               | [386]|
| fGr          | PVA    | Solution blending | 5 wt%           | 2.9                         | 150                          | 177                          | 153                           |                               | [387]|
| GNS          | PVA    | Solution blending | 3 vol%          | 0.12                        | 990                          | 36                           | 166                           |                               | [388]|
| fGr          | PVA    | Solution blending | 0.4 wt%         | 4.8                         | 70                           | 1704                         | 66 at 0.8 wt%                 |                               | [389]|
| fGr          | PVA    | Solution blending | 5 wt%           | 2.9                         | 169                          | 199                          | 170 at 3 wt%                  |                               | [390]|
| GNP          | PA6    | Melt mixing       | 20 wt%          | 1.2                         | 412                          | 54                           |                               |                               | [391]|
| fGr          | PA6    | In situ polymerization | 0.1 wt% | – | 290 | – | 65 | | [392]|
| GNP          | Nylon 6,6 | Solution blending | 10 wt%          | 0.35                        | 120                          | 9                            | 45                            |                               | [393]|
| GNP          | PET/PP | Melt mixing       | 5 phr           | 1.4                         | 38                           | 12                           | 34 at 3 phr                   |                               | [394]|
| GNP          | PP     | In situ polymerization | 4 wt% | 1.6 | 23 | 21 | 12 | | [395]|
| GNP          | PP     | Melt mixing       | 1.7 vol%        | 1.3                         | 54                           | 14                           | –                             |                               | [352]|
| GNP          | PP     | Melt mixing       | 10 wt%          | 1.3                         | 41                           | 13                           | 10                            |                               | [396]|
| PP-g-GNP     | PP     | Melt mixing       | 3 wt%           | 0.66                        | 104                          | 37                           | 8 at 1 wt%                    |                               | [397]|
| GNP          | PP     | Melt mixing       | 0.42 vol%       | 1                           | 74                           | 181                          | 54                            |                               | [341]|
| GNP          | EPDM   | Two roll mill     | 26.7 vol%       | 0.005                       | 710                          | 0.11                         | 405                           |                               | [301]|
| fGNP         | PU     | Solution blending | 2 wt%           | 0.012                       | 216                          | 2.7                          | 17                            |                               | [398]|
| GNP          | PU     | In situ polymerization | 2 wt% | 0.012 | 841 | 10 | 31 | | [399]|
| GNP          | PU     | Solution blending | 1 wt%           | 0.008                       | 122                          | 2                            | 51 at 2 wt%                   |                               | [346]|
| GNP          | TPU    | Solution blending | 3 phr           | 0.45                        | 43                           | 14                           | 22                            |                               | [400]|
| GNP          | TPU    | Solution blending | 15 wt%          | 0.09                        | 1233                         | 15                           | 105 at 2.5 wt%                |                               | [401]|
| GNP          | WPU    | Solution blending | 8 phr           | 0.066                       | 10                           | 0.3                          | 35 at 1 phr                  |                               | [402]|
| GNP          | PLA    | Solution blending | 0.4 wt%         | 0.038                       | 156                          | 250                          | 25                            |                               | [252]|
| GO           | PLA    | Melt mixing       | 0.3 wt%         | 0.12                        | 40                           | 0.3                          | 14                            |                               | [341]|
| GNP          | PA6    | Melt mixing       | 3 wt%           | 1                           | 14                           | 22                           |                               |                               | [341]|
| GNP          | HDPE   | Solution blending | 1 wt%           | 0.36                        | 152                          | 119                          | 19                            |                               | [406]|
| GNP          | HDPE   | Solution blending/ twin screw extrusion | 15 wt% | 1.05 | 59 | 9 | 13 | | [407]|
| GNP          | Bioflex | Melt mixing       | 5 wt%           | 0.14                        | 39                           | 2.3                          | –12                           |                               | [408]|

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Table 2 (continued)

| Graphene type | Matrix | Preparation method | Optimum loading | Matrix modulus $E_m$ (GPa) | Tensile modulus increase (%) | Graphene modulus $E_f$ (GPa) | Tensile strength increase (%) | Fracture toughness increase % | Ref. |
|---------------|--------|--------------------|------------------|----------------------------|-------------------------------|-----------------------------|--------------------------------|-------------------------------|------|
| GNP           | MVQ    | Shear/internal mixing | 8 wt%            | 0.00015                    | 153                          | 0.005                        | 150                            | –                             | [409]|
| GNP           | SBR    | Internal mixing/two-roll mill | 25 phr          | 0.0015                      | 395                          | 0.004                        | 275                            | –                             | [410]|
| GNP           | EPDM   | Two-roll mill       | 10 phr           | 0.0015                      | 88                           | 0.03                         | 2.5 at 2 phr                   | –                             | [411]|
| GNP           | SR     | Solution blending   | 2 phr            | 0.00017                     | 21 (at 100% modulus)         | 0.004                        | 58                             | –                             | [412]|
| GNP           | PET    | Melt blending       | 0.08 wt%         | 0.8                         | 23                           | 463                          | 42                             | –                             | [295]|
| Gr            | PMMA   | In situ polymerization | 0.5 wt%         | 2.1                         | 150                          | 1262                         | 114                            | –                             | [413]|
| fGr           | PVA    | Solution blending   | 0.2 wt%          | 1.48                        | 5                            | 81                           | 23                             | –                             | [414]|
| Gr            | PMMA   | Laminates: sequential transfer | 0.13 vol%      | 2.5                         | 60                           | 1200                         | 27                             | –                             | [214]|
| Gr            | PU     | Solution blending   | 55 wt%           | 0.01                        | 14900                        | 5                            | 48                             | –                             | [415]|
| Gr            | NR     | Latex self-assembly | 8.3 wt%          | 0.0044                      | 1418                         | 0.73                         | 37 at 1.78 vol%                 | –                             | [416]|
| Gr            | NR     | Electrostatic self-assembly | 2.08 vol%   | 0.0013                      | 210 (at 100% elongation)     | 0.1                          | 15 at 0.42 vol%                | –                             | [262]|
| GNR           | PVA    | Solution blending   | 2 wt%            | 0.7                         | 65                           | 47                           | 85                             | –                             | [417]|
| GNR           | SR     | Solution blending   | 2 wt%            | 0.00044                     | 93                           | 0.04                         | 67                             | –                             | [418]|
| GO            | PES    | In situ polymerization | 0.1 wt%         | 0.38                        | 28                           | 210                          | 40 at 0.5 wt%                  | –                             | [338]|
| GO            | Epoxy  | Solution blending   | 0.1 wt%          | 3.0                         | 12                           | 702                          | 13 at 0.5 wt%                  | 63 at 0.5 wt%                 | [419]|
| GO            | Epoxy  | Solution blending   | 1 wt%            | 2.5                         | 24                           | 122.5                        | 14                             | –                             | [350]|
| GO-epeo       | PC     | Solution blending   | 1 wt%            | 1.1                         | 72                           | 171                          | 20                             | –                             | [242]|
| GO            | PSF    | Solution blending   | 1 wt%            | 0.19                        | 16                           | 6                            | 22 at 0.25 wt%                  | –                             | [420]|
| GO            | PMMA   | Melt mixing         | 1 wt%            | 2.2                         | 35                           | 152                          | 21                             | –                             | [304]|
| GO            | PVDF   | Solution blending   | 2 wt%            | 1.4                         | 192                          | 201                          | 92                             | –                             | [421]|
| GO            | PVDF   | Water-assisted extrusion | 0.6 wt%         | 1.4                         | 31                           | 145                          | 12                             | –                             | [422]|
| GO            | PVA    | Solution blending   | 1 wt%            | 7.0                         | 161                          | 2247                         | 37                             | –                             | [423]|
| GO            | PVA    | Solution blending   | 0.3 wt%          | 2.3                         | 150                          | 2335                         | 149                            | –                             | [424]|
| GO            | PVA    | Vacuum filtration   | 5 wt%            | 2                           | 190                          | 162                          | 69 at 3 wt%                    | –                             | [425]|
| f-PVA-GO      | PVA    | Solution blending   | 0.24 vol%        | 2.5                         | 80                           | 836                          | 57                             | –                             | [426]|
| PEI-GO        | PVA    | Solution blending   | 0.5:1 ratio (wt.%) | 3.2                     | 43                           | 401                          | 56                             | –                             | [427]|
| GO            | Nylon 11 | In situ polymerization | 0.5 wt%         | 1.2                         | 38                           | 181                          | –1                             | –                             | [428]|
| PE-g-GO       | HDPE   | Melt mixing         | 3 wt%            | 0.49                        | 21                           | 7.5                          | 22                             | –                             | [429]|
| GO            | PU     | Solution blending   | 3 wt%            | 0.0055                      | 90                           | 0.33                         | 38 at 1.5 wt%                  | –                             | [430]|
| GO            | PU     | In situ polymerization | 3 wt%            | 0.012                       | 275                          | 2                            | 40 at 1 wt%                    | –                             | [337]|
| GO            | PLLA   | Solution blending   | 2 wt%            | 1.56                        | 59                           | 94                           | 52 at 1 wt%                    | –                             | [344]|
| GO            | PS     | Solution blending   | 2 wt%            | 1.83                        | 96                           | 176                          | 89                             | –                             | [344]|
| GO            | PBS    | Solution blending   | 2 wt%            | 0.31                        | 70                           | 22.5                         | 53                             | 100                           | [431]|
| GO            | SBR    | Latex co-agualution | 2 wt%            | 0.001                       | 354 (at 100% elongation)     | 0.19                         | 700                            | –                             | [432]|
| GO            | SBR    | Solution blending   | 5 phr            | 0.0015                      | 433 (at 300% elongation)     | 0.3                          | 316                            | –                             | [433]|
| f-3D-GO       | SBR    | Latex co-agualution | 3.27 vol%       | 0.0026                      | 252 (at 300% strain)         | 0.39                         | 516 at 1.66 vol%               | –                             | [434]|
| GO            | NBR    | Solution blending   | 2 phr            | 0.0023                      | 77 (at 300% modulus)         | 0.18                         | 23                             | –                             | [435]|
| GO            | XNBR   | Latex co-agualution | 2.3 vol%        | 0.0008                      | 262 (at 100% strain)         | 0.09                         | 344 at 1.9 vol%                | –                             | [436]|
| GO            | PEI/XNBR | Layer by layer assembly | 30 cycles (30 wt%) | 0.0012                  | 215                          | 0.016                        | 192                            | –                             | [437]|
| GO            | NR     | Latex compounding/self assembly | 0.7 wt%       | 0.00094                     | 769 (at 200% strain)         | 241                          | 72 at 0.5 wt%                  | –                             | [438]|
| GO            | NR     | Latex mixing        | 1 wt%            | 0.0015                      | 47                           | 0.15                         | 34                             | –                             | [439]|
| GO            | NR     | Solution blending   | 3 wt%            | 0.0016                      | 161                          | 0.18                         | 104 at 0.3 wt%                 | –                             | [256]|
| GO            | NR     | Latex compounding/co-agualution | 5 wt%        | 0.0006                       | 100 (at 100% elongation)     | 0.02                         | 35                             | –                             | [440]|
| GO            | EPDM   | Solution blending   | 0.5 wt%          | 0.055                       | 134                          | 30                           | 52                             | –                             | [345]|

(continued on next page)
Table 2 (continued)

| Graphene type | Matrix | Preparation method | Optimum loading | Matrix modulus $E_m$ (GPa) | Tensile modulus increase (%) | Graphene modulus $E_f$ (GPa) | Tensile strength increase (%) | Fracture toughness increase % | Ref.  |
|---------------|--------|-------------------|-----------------|--------------------------|------------------|-------------------|------------------|------------------|-------|
| GO            | EPDM   | Two-roll mill     | 3 phr           | 0.001                    | 17               | 8                 | –                | –                | [441] |
| GO            | PTT-PTMO | In situ polymerization | 0.7 wt%       | 0.12                      | 15               | 4.4               | 14               | –                | [442] |
| GO            | KGM    | Solution blending | 7.5 wt%         | 6.5                       | 93               | 286               | 152              | –                | [443] |
| fGO           | Epoxy  | Solution blending | 0.5 wt%         | 3.15                      | 19               | 211               | 82% at 0.1 wt%   | 40% at 0.25 wt%  | [266] |
| fGO           | Epoxy  | Solution blending | 0.5 wt%         | 3.15                      | 14               | 175               | 49 at 0.1 wt%    | –                | [444] |
| fGO           | PET    | Solution blending | 0.5 wt%         | 0.48                      | 62.5             | 118.5             | 90               | –                | [445] |
| fGO           | PLLA   | Solution blending | 1 wt%           | 1                         | 11.3             | 34                | 22               | –                | [446] |
| fGO           | PI     | In situ polymerization | 0.3 wt%       | 1.92                      | 739              | 9468              | –                | –                | [447] |
| fGO           | PI     | In situ polymerization | 3 wt%         | 1.35                      | 1418             | 1278              | 892              | –                | [278] |
| fGO           | PVA    | Solution blending | 2 wt%           | 0.16                      | 231              | 44                | 103              | –                | [448] |
| fGO           | PDMS   | Solution blending | 3 wt%           | 0.00025                   | 71               | 55                | –                | –                | [449] |
| fGO           | PP     | Melt mixing       | 1 wt%           | –                        | 47               | –                 | 29               | –                | [450] |
| fGO           | PP     | Melt mixing       | 5 wt%           | –                        | 43               | –                 | 18 at 0.5 wt%    | –                | [451] |
| fGO           | PU     | In situ polymerization | 2 wt%         | 0.0085                    | 364              | 3                 | 100              | –                | [452] |
| fGO           | TPU    | Solution blending | 50 wt%          | 0.0096                    | 3389             | 1.3               | 40 at 3 wt%      | –                | [453] |
| rGO           | Epoxy  | Solution blending | 0.5 phr         | 2.4                       | 11               | 110               | 32 at 0.25 phr   | 63 at 0.25 phr   | [454] |
| rGO           | Epoxy  | In situ polymerization | 2 wt%         | 0.48                      | 70               | 34                | 400 at 1.5 wt%   | –                | [455] |
| rGO           | Epoxy  | Solution blending | 0.2 wt%         | 2.91                      | 6                | 173               | 7                | 51               | [456] |
| rGO          | PMMA   | Emulsion polymerization | 1 wt%         | 3.12                      | 42               | 265               | 15               | –                | [457] |
| rGO          | PMMA   | In situ polymerization | 2 wt%         | 0.75                      | 40               | 31                | 17 at 1 wt%      | –                | [284] |
| rGO           | PVA    | Wet spinning      | 2 wt%           | 5.4                       | 294              | 1036              | 244              | –                | [458] |
| rGO           | PVA    | Solution blending | 27.2 wt%        | 0.6                       | 408              | 19                | 535              | –                | [459] |
| rGO           | PE     | Solution blending | 3 wt%           | 1.4                       | 119              | 155               | 123              | –                | [460] |
| rGO           | PE     | In situ polymerization | 5.2 wt%       | 0.23                      | 170              | 15                | 57               | –                | [287] |
| rGO           | PE/OPE | Solution blending | 3 wt%           | 0.0016                    | 500              | –                 | –                | –                | [461] |
| rGO           | LLDPE  | Solution blending | 3 wt%           | 0.005                     | 147              | 0.86              | –                | –                | [462] |
| rGOONRs       | PP     | Solution blending | 0.3 wt%         | 0.28                      | 98               | 188               | 15               | –                | [463] |
| rGO           | PF     | In situ polymerization | 0.5 wt%       | 1                        | 64               | 2                 | 65               | –                | [464] |
| rGO           | PC     | Solution blending | 0.25 wt%        | 1.8                       | 11               | 116               | 2                | –                | [465] |
| rGO           | PHO    | Solution blending | 2.5 vol%        | 0.0045                    | 590              | 1                 | 9                | –                | [466] |
| rGO           | poly   | Solution blending | 5 phr           | 0.001                     | 112              | 0.04              | 237              | –                | [467] |
| rGO ONRs      | PU     | In situ polymerization | 2 wt%         | 0.011                     | 197              | 2.3               | 242              | –                | [334] |
| rGO           | PU     | In situ polymerization | 0.94 vol%     | 0.01                      | 500              | 5.3               | 50 at 0.24 wt%   | –                | [468] |
| rGO           | WPU    | Solution blending | 3 wt%           | 0.028                     | 2028             | 39                | 785              | –                | [469] |
| rGO           | TPU    | Solution blending | 2 vol%          | 0.033                     | 181              | 0.2               | –                | –                | [470] |
| rGO           | SBR    | Latex compounding | 7 phr           | 0.0016                    | 552              | 0.25              | 992              | –                | [471] |
| rGO           | NR     | Latex co-       | 5 wt%           | 0.001                     | 320 (at 300%    | 0.13              | 403              | 18               | [472] |
| rGO           | NR     | coagulation/solution | 30 phr         | 0.0001                    | 29900             | 8                 | 203              | –                | [473] |
| rGO           | EVOH   | Solution blending | 4 wt%           | 0.27                      | 300              | 42                | 180              | –                | [474] |
| rGO           | PVA    | Solution blending | 0.7 wt%         | 4                         | 37               | 379               | 40               | –                | [475] |
| rGO           | PVA    | Solution blending | 1 wt% (reduced | 2.1                       | 66               | 282               | 45 (reduced for 12 h) | –                | [476] |
| rGO           | OPBI   | Solution blending | 40 wt%          | 2.9                       | 201              | 33                | 97 at 20 wt%     | –                | [477] |
| rGO           | CHGEL  | Solution blending | 30 wt%          | 0.008                     | 487              | 8                 | 313              | –                | [478] |
| rGO           | CHI    | Solution blending | 7 wt%           | 2.4                       | 183              | 128               | 134 at 6 wt%     | –                | [479] |
| frGO          | PP     | Solution blending | 0.5 wt%         | 1.15                      | 16.5             | 65                | 19               | –                | [265] |
| frGO          | PVA    | Solution blending | 3 wt%           | 0.06                      | 59               | 167               | 31 at 1 wt%      | –                | [480] |
types of graphene. It can also be seen that the stiffer the matrix, the higher the effective modulus of the filler, a fact that also depends on additional parameters such as the orientation, the interphase, the functionalization and others. Moreover, it is obvious that there is a large number of works in soft matrices with stiffness in the order of a few MPa (elastomers) and stiffer

Table 2 (continued)

| Graphene type | Matrix | Preparation method          | Optimum loading | Matrix modulus $E_m$ (GPa) | Tensile modulus increase (%) | Graphene modulus $E_f$ (GPa) | Tensile strength increase (%) | Fracture toughness increase % | Ref.  |
|---------------|--------|-----------------------------|-----------------|---------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------|
| frGO          | PI     | In situ polymerization      | 1 wt%           | 1.1                       | 151                           | 459                         | 181                           | -                           | [481] |
| frGO          | PVDF   | Solution blending           | 5 wt%           | 1.0                       | 585                           | 270                         | 317 at 1 wt%                 | -                           | [482] |

Fig. 25. Modulus of graphene as a function of the modulus of the matrix. Data were obtained from the extensive literature with values of $E_f$ and $E_m$ listed in Table 2.
matrices (thermoplastics-thermosets), while the category of materials with average stiffness ranging from 10 MPa to 1 GPa (e.g. thermoplastic elastomers) seems underrepresented. It remains a challenge to be able to analyse fully the relationships shown in the plots in Fig. 25 that may hold the key to understanding the mechanisms of reinforcement in graphene-based nanocomposites.

7.3.3. Raman band shifts for bulk composites

In situ Raman spectroscopy combined with deformation, that was described for model composites, can be also applied in the case of bulk composites. The downshift of the characteristic graphene bands can be an indicator of the stress transfer efficiency between the fillers and the matrix, while the slope is an indication of the effective modulus of the reinforcement. A small number of research groups have applied the specific procedure in bulk composites [210,250,304,324,349–352] reinforced with either GO or GNP. Li et al. [349] studied interfacial stress transfer in poly(vinyl alcohol) nanocomposites reinforced with graphene oxide. From the bending procedure it was found out that the downshift of the D band for the nanocomposites ($\Delta \omega_D/\Delta \varepsilon$) was around $-8 \text{ cm}^{-1}/\%$ (Fig. 26) and given the fact that graphene with a modulus of 1050 GPa has a D band shift rate of $-30 \text{ cm}^{-1}/\%$ [353], the effective modulus of the samples was calculated using the following expression:

$$\text{effective GO modulus} = \frac{d \omega_D}{d \varepsilon} \times \frac{1050 \text{ GPa}}{-30 \text{ GPa}} = 34.8 \text{ GPa} \quad (7.11)$$

where 0.34 and 0.84 are the thicknesses of monolayer graphene and graphene oxide (in their study). The effective modulus of GO from the Raman D band shift rate per unit strain was found to be in the order of 120 GPa. It should also be stated that the theoretical value of the simplified Gruneisen parameter $\gamma$ for free-standing graphene was chosen as $\gamma = 2.7$ [353].

Shang et al. [250] studied a similar PVA/GO system, where the GO was exhibiting a crumpled and folded morphology at low filler contents (0.3 vol%). The authors monitored the downshift of the G band of GO, which exhibited a characteristic

![Fig. 26. (a) Downshift of the D band of GO for the nanocomposites filled with 5 wt% GO. Reprinted (adapted) with permission from [349]. Copyright 2013, American Society of Chemistry. (b and c) Raman shifts of the G$^+$ and G$^-$ bands in PVA reinforced with short and long GO flakes. Reprinted from [250]. Copyright 2015, with permission from Elsevier. (d) Dependence of the effective modulus of the GNP in a PP/GNP nanocomposite on the different experimental procedures, with increasing GNP loading. Reprinted from [352]. Copyright 2016, with permission from Elsevier.](image)
broadening, indicative of defects and of the disruption of the conjugated π systems due to the presence of the functional
groups. The G band was fitted with 3 components; G+, G− and D’ peaks and the downshift of the G+ and G− peaks was
observed with increasing strain, while as expected at higher strains, a plateau was observed in the downshift versus strain
graphs (Fig. 26b and c). In accordance with the conclusions reported by Gong et al. [178] the larger GO (l-GO) flakes can bear
higher loads before the downshift reaches the plateau, while the shift rates were almost double than the ones of the short GO
(s-GO) flakes for the G− band and three times higher than the ones for the G+ band (Fig. 26b and c). Both studies [250,349] are
excellent examples that the in situ Raman deformation procedure is not only useful in model composites but it can provide
important information that can lead to significant conclusions regarding the effective modulus of the reinforcement and the
efficiency of stress transfer from the flakes to the matrix.

In the report of Ahmad et al. [352], the authors calculated the effective modulus of GNPs in polypropylene (PP) through a
combination of tensile and dynamic mechanical testing, along with Raman spectroscopy. It was revealed that the effective
modulus obtained from the Raman 2D band shift is independent of the loading of the filler, whereas the values of $E_l$ obtained
from the tensile and storage modulus, decreased with increasing loading (Fig. 26d). This effect is the direct consequence of
the uniform strain applied in nanocomposites. It has already been shown that Raman band shift rate with increasing strain, is
independent of the loading of the filler, while it depends on the volume filler fraction when the stress increases [354]. It
should also be taken into account that the laser spot of Raman is usually in the order of 1–2 μm, while the GNP flakes
are significantly larger, an indication of the measurement of the deformation of individual flakes, which is not affected by
the GNP content. On the other hand, the tensile and dynamic mechanical tests offer information from the whole volume
of the bulk composite, which means they are sensitive to factors that were discussed in previous parts of this review such
as the nanoparticle orientation, thickness or length and are known to reduce significantly the modulus of the material, com-
pared to monolayer graphene.

In another recent report, Li et al. [355] investigated the effect of adding GNPs to natural rubber (NR) and they benchmarked
the behaviour against the addition of carbon black. They found that the GNPs were up to three times more effective
on increasing the stiffness of the natural rubber than the carbon black and that their effective filler modulus was of the order
of 100 MPa. Importantly, they also measured ($\varepsilon_{\text{f}}$) for the same GNP-filled materials. In this case, the band shifts were
rather scattered and very small, typically in the order of only –1 cm$^{-1}$ for 100% strain. Nevertheless, this is also consistent
with an effective Young’s modulus of 125–300 MPa for the GNPs in the natural rubber ($E_m$ ~ 1 MPa). This observation rein-
forces the correlations between $E_l$ and $E_m$ shown in Fig. 25. We will only be able to fully understand the mechanisms of rein-
fforcement once such correlations are backed up by a sound theoretical analysis.

8. Hybrid graphene composites

A promising strategy that has been increasingly explored in the literature for the preparation of graphene-based compos-
ites, is the use of hybrid fillers, that consist of graphene and a second inorganic material. The combination of the two may
prove advantageous for the final product since the ultimate properties can be a result of additive or synergistic effects
between the fillers. Moreover, the hybridisation procedure can counterbalance some of the disadvantages of a specific filler,
while it may also enhance the interactions with the matrix depending on the functionalization route. Therefore, the multi-
functionality is a very important parameter for the preparation of hybrid composites since the combined properties of the
two fillers can lead to the production of a new material with quite a diverse set of properties. Furthermore, the cost of the
final product can be reduced since well-established microscale reinforcements such as carbon and glass fibres can be com-
bined with small amounts of graphene and produce hybrid composites where the stress can be transferred from the micro-
scale to the nanoscale reinforcement, improving the ultimate mechanical and other properties.

8.1. Hybrid graphene/nanofiller nanocomposites

The bonding between the individual fillers plays a very important role on the final physicochemical properties of a composite
reinforced with hybrid fillers. Several strategies have been explored in literature in order to increase the affinity between the
fillers such as chemical functionalization, solution blending, growth on top of each other, mechanical mixing, etc. Moreover,
as has been clearly stated in this review, graphene is known to form agglomerates very easily due to its high specific surface
area and van der Waals interactions, so one of the methods that have been explored for the avoidance of this phenomenon,
is the decoration of graphene with other nanomaterials. Of course, this can come at a cost, since the functionalization of gra-
phene (or the use of GO) for the enhanced bonding with other nanomaterials expands the reactive sites of the graphene and
ultimately leads to the formation of significantly fewer covalent bonds between the matrix and the final hybrid filler.

The preparation strategies for the bulk hybrid composite are more or less the same as the ones that have been already
described earlier. Yang et al. [356] prepared hybrid epoxy composites reinforced with 0.1 wt% multi-walled carbon nan-
tubes (MWCNTs) and 0.9 wt% multi-graphene platelets (MGPs) for the improvement of the mechanical properties and ther-
mal conductivity. One set of samples combined amine-functionalized-MWCNTs and MGPs for the formation of hybrid
structures, while a second set of samples was prepared with un-functionalized MWCNTs and MGPs (Fig. 27). As expected,
the functionalization of MWCNTs enhanced the bonding between the fillers and led to improved ultimate mechanical prop-
erties. The combination of a 2D-filler (MGPs) and 1D-filler (MWCNTs) led to the formation of a 3D structure which inhibited
face-to-face aggregation of the MGPs and resulted in a filler with a high surface area. Compared to the un-functionalized hybrid filler, the tensile strength and the tensile modulus both increased, while interestingly the elongation increased as well, as a result of the presence of the amines, which form a highly-crosslinked structure. Finally, thermal conductivity was increased by more than 50% compared to the pristine hybrid filler since the functionalized MWCNTs inhibited aggregation of MGPs and formed a pathway promoting phonon diffusion.

Lin et al. [357] prepared silica/reduced graphene oxide (SiO2/rGO) hybrids by an electrostatic method and then blended the hybrid filler mechanically in a two-roll mill with a styrene butadiene rubber matrix. The hybrid materials were better dispersed than the individual ones, while the interactions with the matrix were also stronger. This resulted in dramatic increases in the modulus, tensile strength and tear strength and revealed that these materials can be considered as alternatives for green tyre applications and high-performance rubber products.

In situ Raman spectroscopy combined with a bending procedure has been also employed for a set of graphene oxide (GO)/attapulgite (ATP) hybrid epoxy composites, where GO was added at 0.1 or 0.2 wt% and ATP at 1 or 2 wt% [358]. The authors studied the downshift of the D band with increasing strain (up to 0.8%) for the evaluation of the stress-transfer efficiency. Increasing the filler content of ATP from 1 to 2 wt% leads to lower shift rates, as a result of the shielding of the functionality of GO due to the higher loading of ATP, which in turn causes a degradation of the interfacial adhesion between the components of the system (and lower shift rates). Interestingly, the results also showed that the sample filled with 0.2 wt% GO and 1 wt% ATP exhibited higher shift rates compared to the sample filled with only 0.2 wt% GO (−6.4 cm⁻¹/% over −5.4 cm⁻¹/%), which can be an indication of synergy between the components of the hybrid system.

8.2. Graphene/fibre hybrid composites

Fibre-reinforced composites are already considered to be very attractive materials for replacing conventional metals in several high performance applications such as aerospace, automotive, marine and construction industries. The ultimate properties of fibre composites are dictated by the strength of the interface between the matrix and the fibre and this is an area where adding graphene-based materials can make a real difference. Moreover, the use of long, micron sized fibres can confine nanoparticles in the interfacial region, creating this way a localized presence in the area where stress transfer or electron/phonon conduction takes place and reducing in this way the quantity of nanoparticles needed for reinforcement.

In the work of Yavari et al. [359] the authors prepared graphene/glass-fibre/epoxy composites by directly spraying graphene onto glass fibres or by infiltrating graphene into an epoxy resin matrix. Fatigue tests revealed that the hybrid filler attributed an enhancement of the flexural bending fatigue by over three orders of magnitude with very low weight fractions of graphene. In a different report from Pathak et al. [360] a hybrid carbon-fibre/graphene-oxide/epoxy composite was prepared in two steps: initially epoxy was reinforced with graphene oxide and then the carbon fibre fabric was impregnated with the modified epoxy resin by compression molding (Fig. 28). The results showed that the flexural strength increased by 66%, while the modulus increased 72%. Moreover, the interlaminar shear strength increased by 25% at 0.3 wt% of GO, as a result of the interlocking and hydrogen bonding between the components of the system.
Mannov et al. [361] investigated cross-ply laminates with carbon (CF) and glass fibres (GF) in which different loadings of thermally-reduced graphene oxide were introduced, in order to improve the toughness of the hybrid composites. The results showed that the presence of TrGO toughened the matrix and led to less impact damage and an increased residual compressive strength. Interestingly, the TrGO-reinforced CF epoxy displayed an increase of the damage area compared to the unmodified CF epoxy, indicating that a higher proportion of the impact energy is dissipated in the upper delamination layers which leads to less damage expansion in the specimen. Knoll et al. [362] looked into the fatigue performance of carbon fibre reinforced epoxy after the introduction of few layer graphene (FLG) and multi-walled carbon nanotubes (MWCNTs). The fatigue lifetime was found to be most pronounced for the FLG at high fatigue loads with a 15-fold improvement and accordingly the fatigue degradation process was significantly slower. The authors also studied in detail the dominant damage mechanism for each nanofiller. The higher fatigue life of FLG compared to MWCNTs was attributed to the high surface area and the layer separation during failure.

Finally, in a recent work from our group, graphene nanoplatelets were combined with glass fibres for the reinforcement of a polypropylene matrix [363]. The matrix was initially reinforced with 20 wt% glass fibres and GNPs were introduced in loadings ranging from 5 to 20 wt%. At the highest filler content (20 wt% GNP and 16 wt% GF) the tensile modulus of the matrix was three times higher than its original modulus, while the tensile strength was also significantly improved. The in situ Raman bending procedure was applied in the hybrid system and the higher shift rates compared with the conventional PP/GNP samples revealed that the stress transfer efficiency was better for this set of samples (Table 3). These results were consistent with the tensile testing, as the hybrid samples performed better than the conventional composites.

Similarly to the majority of “conventional” graphene-based composites, the elastic modulus of hybrid materials increases with increasing filler content, while the ultimate strength is more sensitive to aggregation phenomena at lower filler concentrations. Details of the mechanical properties of a number of graphene-based hybrid polymer composites reported in the literature are listed in Table 4.

### Table 3
Average Raman 2D band shift rates for the composite samples filled with GNP and for the hybrid samples reinforced with GF/GNP [363].

| Sample       | Shift rate (cm⁻¹/%) | Sample       | Shift rate (cm⁻¹/%) |
|--------------|---------------------|--------------|---------------------|
| PP-GNP5      | −5.3 ± 0.5          | PP-GF19-GNP5 | −6.9 ± 0.8          |
| PP-GNP10     | −4.9 ± 0.4          | PP-GF18-GNP10| −6.3 ± 0.7          |
| PP-GNP20     | −4.7 ± 0.5          | PP-GF16-GNP20| −6.1 ± 1.3          |
|              |                     | PP-GF10-GNP10| −5.9 ± 0.9          |
## Table 4
Mechanical properties of graphene-based hybrid composites.

| Filler #1  | Content | Filler #2  | Content | Hybrid filler content | Filler bonding | Matrix  | Preparation method          | Modulus increase (%) | Tensile strength increase (%) | Ref.   |
|------------|---------|------------|---------|-----------------------|----------------|---------|----------------------------|----------------------|-------------------------------|--------|
| GNP        | 0.26 wt % | MWCNT | 0.24 wt % | –                  | Mechanical mixing | Epoxy   | Three roll mill           | 14                   | 20                            | [483]  |
| GNP        | 0.26 wt % | MWCNT | 0.24 wt % | –                  | Growth of CNT on GNP surface (CVD) | Epoxy   | Three roll mill           | 40                   | 36                            | [484]  |
| GNP        | 0.1 wt%  | MWCNT | 0.1 wt%  | –                  | Solution bonding | Epoxy   | Solution blending          | 18                   | 12                            |        |
| GNP        | 0.9 wt%  | MWCNT | 0.1 wt%  | –                  | Solution bonding | Epoxy   | Solution bonding          | 27                   | 35                            | [356]  |
| GNP        | 0.5 wt%  | GF     | 15 wt%   | –                  | Solution bonding | Epoxy   | Solution bonding          | 45                   | 19                            | [485]  |
| GNP        | 0.2 wt%  | CB     | 24 wt%   | –                  | Solution bonding | UHMWPE  | Solution bonding          | 37                   | 31                            | [486]  |
| GNP        | 0.5 wt%  | GF     | 15 wt%   | –                  | Two roll mill    | EPDM    | Two roll mill             | 209                  | 143                           | [411]  |
| GNP        | 20 wt%   | GF     | 16 wt%   | –                  | Melt mixing      | PP      | Melt mixing               | 126                  | 16                            | [487]  |
| GNP        | 0.26 wt % | MWCNT | 0.75 wt% | –                  | Solution bonding | Epoxy   | Solution blending          | 36                   | 16                            | [363]  |
| GNP        | 2 wt%    | Co(OH)2| 4 wt%    | –                  | Solution bonding | ABS     | Solution blending         | 137                  | 110                           | [488]  |
| GNP        | 1 wt%    | NC     | 1 wt%    | –                  | Liquid phase exfoliation | PVA    | Solution blending          | 50                   | 12                            | [490]  |
| fGr        | 5 wt%    | fMWCNT | 5 wt%    | –                  | Solution bonding | Epoxy   | Solution blending          | 98                   | 12                            | [491]  |
| GO         | 0.2 wt%  | ATP    | 1 wt%    | –                  | Solution bonding | Epoxy   | Solution blending          | 36                   | 16                            | [358]  |
| GO         | –        | fSiO2  | –        | 0.75 wt%            | Solution bonding | Epoxy   | Solution bonding          | 8 (at 1 wt% total filler) | 45                            | [492]  |
| GO         | 1 wt%    | SiO2   | –        | 20 wt%              | Solution bonding | Epoxy   | Solution bonding          | 41                   | 35 at 10 wt% SiO2–GO         | [493]  |
| GO         | –        | SiO2   | –        | 1.5 wt%             | Solution bonding | Epoxy   | Solution bonding          | 31                   | (at 10 wt% SiO2–GO)          | [494]  |
| GO         | 5 wt%    | SCF    | –        | –                  | Wetting of SCF through GO sizing | Epoxy   | Solution blending          | 10 (compared to EP/SCF)   | 34 (compared to EP/SCF)      | [495]  |
| GO         | 0.2 wt%  | MWCNT  | 0.06 wt% | –                  | Solution bonding | Epoxy   | Solution bonding          | 11                   | 12 at 0.04 wt% MWCNT         | [496]  |
| GO         | 0.3 wt%  | CF     | –        | –                  | Impregnation/compression molding | Epoxy   | Impregnation/compression molding | 72                   | 66                            | [360]  |
| GO         | –        | Kevlar Fibres | –        | 0.7 wt%            | Solution bonding | PMMA   | Solution bonding          | 71                   | 85                            | [497]  |
| GO         | –        | Al     | –        | 1 wt%              | Sol-gel process   | PI      | Solution bonding          | 12                   | 25                            | [498]  |
| GO         | –        | SiO2   | –        | 20 wt%             | Electrostatic assembly | PDVF    | Solution bonding          | 34                   | 12                            | [499]  |
| GO         | 0.5 wt%  | SCF    | 12.5 wt% | –                  | Solution bonding | PES     | Solution bonding          | 185                  | 38                            | [500]  |
| GO         | 0.5 wt%  | GF     | 3 wt%    | –                  | Solution bonding | PES     | Melt mixing               | 80                   | 10                            | [501]  |
| GO         | 0.9 wt%  | MMT    | 0.3 wt%  | –                  | Solution bonding | PVA     | Solution bonding          | 43                   | 58                            | [502]  |
| GO         | 0.3 wt%  | CF     | 1 wt%    | –                  | Solution bonding | PVA     | Solution bonding          | 106                  | 80 at (3 wt% MWCNT and 6 wt% GO) | [503]  |
| GO         | 0.215 wt% | CF    | 0.3 wt%  | –                  | Electrophoretic deposition | PU      | Pre-polymerization         | 684                  | 36 at 0.1 wt% GO              | [504]  |
| GO         | 2.15 wt % | MWCNT | 2.15 wt % | –                  | Solution bonding | NR      | Solution bonding/melt mixing | 100                  | 80                            | [505]  |
| rGO        | –        | SiO2   | –        | 30 phr             | Electrostatic assembly | SBR     | Two roll mill             | 170 (at 300% strain) | 1204                           | [357]  |
| Graphene foam | –      | CF     | 10 wt%   | –                  | Shear mixing/mechanical pressing | PDMS    | Shear mixing/mechanical pressing | 185                  | 63                            | [506]  |
9. Conclusions and outlook

The mechanical properties of graphene and graphene-based nanocomposites have been reviewed. It has been shown that the possibilities and capabilities of this family of materials for advanced engineering applications are practically endless due to their enhanced properties attributed from the presence of multifunctional graphene-based nanofilms. The majority of the production routes and properties of graphene and graphene oxide have been defined, while once again it has been exhibited how important Raman spectroscopy can be for fundamental and applied studies of graphene and its nanocomposites. A detailed analysis of the status on the use of Raman spectroscopy for the investigation of mechanical properties of graphene based materials has also been performed by providing several literature examples and subsequent interpretation of the results. The effectiveness of this method on the evaluation of the stress transfer efficiency between the filler and the matrix and the calculation of the effective modulus of the filler in both bulk and model composites has been exhibited clearly. Moreover, the use of graphene in bulk composites has been explored. The advances in the preparation strategies have been described, while the literature has been analysed extensively for the evaluation of the reinforcement efficiency of each graphene type in a range of matrices, with different preparation routes. Detailed analysis of this literature has revealed an dependence between the efficiency of reinforcement and the modulus of the matrix used.

It should be stated that there are still several challenges to be tackled before industry can proceed with the mass production of graphene nanocomposites. For example, the scale up of the production of high-quality graphene is a major issue which is always going to be reflected on the ultimate properties of the materials. Based on the findings presented earlier, the best quality graphene for use in nanocomposites can be considered to be material with the largest aspect ratio and with a thickness of few layers. For the successful production of advanced composites the dispersion of the filler should be homogeneous so as not to form aggregates that can act as failure points during the testing procedures. The bonding between the filler and the matrix must also be strong, so that efficient stress transfer can take place. Moreover, the filler should not exhibit characteristics that limit its potential such as wrinkles, impurities, a small lateral size or defects. The major route followed for the increase of interactions between the filler and the matrix is the functionalization of graphene and sometimes the use of compatibilisers, which is another drawback for the scale up of the production, since it demands the excessive use of chemicals and solvents. A very interesting and promising route for counterbalancing some non-desired properties of graphene in composites is the use of hybrid fillers, i.e. a combination of graphene and an inorganic filler such as MWCNTs, BN, MoS2 and others. Despite these challenges, the multi-functionality of such materials is difficult to be ignored by industry and commercial graphene products such as tennis racquets and cycle tyres are already finding their way to consumers. Taking this into account, the commercial impact of graphene nanocomposites is quite likely to increase in the future and graphene is going to be transformed from a material ideal for fundamental studies by scientists leading to new physics, to an engineering material offering important solutions for industrial and consumer needs.

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