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Mechanical properties of aerospace epoxy composites reinforced with 2D nano-fillers: current status and road to industrialization

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High-performance epoxy composites find application in the aerospace industry. Although epoxy is a high-performance polymer, its fracture toughness is compromised due to its highly cross-linked nature. Nanomaterials such as carbon nanotubes (CNTs), graphene derivatives, and inorganic 2-dimensional (2D) nanomaterials are being explored to improve epoxy composites' mechanical properties. Graphene is one of the most popular 2D nano-reinforcing agents for epoxy composites. Following graphene discovery, the research community's attention was brought to various other few-atom thick 2D nanomaterials. Hence, apart from graphene, inorganic nanosheets such as transition metal dichalcogenides (TMDs), hexagonal boron nitride (hBN), *etc.*, are also being studied as modifiers for enhancing the mechanical performance of epoxy composites. Graphene, TMDs and hBN are known to possess a high aspect ratio, high specific surface area and inherently high mechanical strength and stiffness, contributing to a stronger and tougher composite. Despite that, the challenges associated with these nanomaterials, such as dispersion issues, lack of standardization, underlying health hazards, *etc.*, have hampered their commercialization. It has been long past a decade since the discovery of graphene, yet there are concerns regarding the lab to industry scale-up, and health and environmental hazards associated with nanomaterials for the fabrication of aerospace composites. This review offers a comprehensive literature survey and a perspective into the possible ways of bridging the gaps between the laboratory research and industrialization of 2D nanosheet-filled epoxy composites.

1. Introduction

Metal alloys, especially aluminum alloys, have been an indispensable part of the aerospace industry for a long time. A large portion of the product range offered by aircraft manufacturers

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still comprises of metal aircraft. However, since the last decade, there has been a shift towards polymer composites. Modern planes such as Boeing 787 and Airbus A380, which came into service in the last decade, utilize more than 50% by weight carbon fiber reinforced epoxy composites in the aircraft fuselage, wings and empennage assemblies. In comparison to metals, polymer composites, especially epoxy composites, offer several advantages. They possess higher corrosion resistance, better strength to weight ratio, require fewer sub-assemblies, consume less fuel due to reduced weight, offer easier repair and maintenance, *etc.* However, there are some limitations associated with epoxy composites. Like most other polymers, epoxy is also thermally and electrically non-conducting, which leads to its inability to deal with electromagnetic interference and lightning strikes. Another limitation of epoxy is that it is highly brittle due to its heavily cross-linked network. Aircraft structures undergo extreme thermal cycles, mechanical load and fatigue and need to have good fracture toughness so that catastrophic failure does not occur. Researchers are continuously trying to improve the mechanical properties of epoxy composites, focusing on fracture toughness. Many toughening agents such as rubber,[1,2] thermoplastic polymer particles, silica nanoparticles,[3] and nanoclay[4] have been explored to enhance epoxy's mechanical properties. Several researchers have been exploring CNTs,[5,6] graphene, and more recently, inorganic 2D nanomaterials[7,8] for the improved mechanical performance of epoxy composites. Amongst these, 2D nanomaterials are popular due to their high aspect ratio and inherently high mechanical strength.[9]

Many review articles have been published on the subject of nano-fillers for epoxy. Domun *et al.*[10] comprehensively reviewed the status of epoxy composites reinforced with single and multiwalled CNTs, graphene, nano-silica and nano-clay. The authors summarized the effect of these nano-fillers on the tensile and fracture properties of epoxy composites. They pointed out the lack of uniformity in the composite fabrication methods, filler functionalization, and dispersion techniques used, restricting the understanding of the composites' mechanical properties. The lack of suitable quantitative methods to assess filler dispersion and filler-matrix interaction was also mentioned. A review article by Marouf *et al.*[11] discussed and compared the effect of one, two and three-dimensional nano-fillers on the fracture properties of epoxy composites. The underlying toughening mechanisms in binary and ternary epoxy composites reinforced with nanofillers such as nano-silica, nano-rubber, CNTs, nanoclay and graphene were discussed in detail in this article. Szeluga *et al.*[12] reviewed graphene fillers' effect on the mechanical, thermal, electrical and flame retardant properties of epoxy composites. The effect of filler size, degree of exfoliation and functionality on the properties of epoxy composites was summarized. The authors pointed out that there is insufficient literature to assess the filler-matrix interaction accurately. Atif *et al.*[13] reviewed epoxy composites reinforced with graphene. They established a correlation of the filler size, morphology, and functionalization extent with the final epoxy composites' mechanical, thermal, and electrical properties. The authors pointed out the lack of consensus regarding graphene's effect on the properties of epoxy nanocomposites.

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In a review by Kulkarni *et al.*,[14] the authors described the covalent and non-covalent functionalization approaches for surface modification of graphene. The authors discussed the effects of processing protocols, filler dispersion, and filler surface modification on graphene–epoxy composites' electrical, mechanical, and thermal properties. Singh *et al.*[15] reviewed graphene, CNTs, and graphene/CNT hybrid reinforced epoxy composites. The influence of the filler's type and functionality on the mechanical, thermal, electrical and flame-retardant properties of epoxy composites was discussed. The various applications of such composites, especially in aircraft body, electro-magnetic shielding, corrosion-resistant coatings, *etc.*, were discussed.

Research groups worldwide have extensively worked on epoxy reinforced with graphene and inorganic 2D nanofillers and have produced promising results in terms of the mechanical and thermomechanical performance of these composites. Despite the abundant literature on 2D nanomaterial-filled epoxy resins, it has still not graduated from the laboratory to the aircraft industry. Hence, a perspective is needed in terms of the research conducted in this field, its challenges, and the possible solutions to these challenges.

The review articles on 2D nanofiller reinforced epoxy composites available so far have majorly taken into consideration graphene and its derivatives. To the best of our knowledge, the status of inorganic 2D nano-fillers, especially TMDs and hBN and their various organic and inorganic multiscale hybrids, which are being extensively explored to reinforce epoxy composites, has not been reviewed yet. Many authors have discussed the problems associated with the processing and dispersion of nano-fillers. However, successful commercialization of such epoxy nanocomposites is being hampered by challenges such as health hazards, lack of standardization of nanomaterials, and effective scale-up of technology, which have not been discussed in the review articles so far.

The current review comprises an exhaustive literature survey on epoxy composites loaded with 2D nanomaterials, including graphene and its derivatives, TMDs, hBN and other 2D inorganic nanomaterials and their hybrids. Fig. 1 shows a schematic of the structure of graphene and TMDs and their multiscale hybrids. However, since this review focuses on 2D fillers, only 2D–2D hybrids have been covered in detail. The effect of filler size, filler chemistry, loading level and dispersion state on the mechanical and thermomechanical properties of epoxy resin has been discussed. Furthermore, a holistic view of the major challenges of using 2D nanosheets as potential fillers for epoxy resin has been brought to light. This review tries to rationalize the projected potential of graphene and other 2D materials used in the fabrication of epoxy composites and highlights the gap between the laboratory and industry. The difficulties associated with the standardization and scale-up, and health hazards related to the use of 2D nanomaterials have also been discussed. Fig. 2 schematically summarizes the idea behind the review article, covering the types of 2D fillers used to make epoxy composites, their applications in the aerospace industry and various challenges around such nanocomposites.

2. 2D nano-materials

This section briefly touches upon the various synthesis methods of 2D nanosheets such as graphene, TMDs, hBN, *etc.*, along with their basic properties and applications. Such 2D nanomaterials are often subjected to surface modification to improve their performance as fillers in composite materials. These functionalization strategies have also been discussed.

2.1 Graphene

Graphene is a single layer of carbon atoms arranged in a 2D honeycomb lattice. Graphene is the building block of 0D (fullerenes), 1D (CNTs) and 3D graphitic materials.[16] Monolayer graphene displays a Young's modulus of 1 TPa and intrinsic tensile strength of 130 GPa.[9] Graphene exhibits a large theoretical surface area of 2630 m^2 g^{-1}, unique optical properties, ultrahigh electronic mobility (>200 000 cm^2 V^{-1} s^{-1})[17,18] and high thermal conductivity (>5000 W m^{-1} K^{-1}).[19] These excellent properties make graphene a go-to material for myriad applications, including sensors, conductive films, polymer composites, photonics, *etc.*[20] The robust and flexible nature of graphene opens possibilities for its surface modification.[21] Table 1 summarizes the inherent mechanical properties of some nanofillers. The popularity of graphene extends to several research areas. Due to its versatile nature, it is used in the biomedical industry,[22] sensors and electronic devices,[23,24] wastewater treatment,[25] optical applications,[26,27] thermal conductivity applications,[28] polymer composites *etc.*

2.2 Inorganic 2D materials

As compared to their bulk equivalent, 2D materials often possess unique properties due to their high aspect ratio and tunable surface properties. They are known to be mechanically robust (Table 1). Researchers are extensively studying other layered 2D materials having structural similarity to graphene to explore their unusual properties and applications. Falling in this category of 2D materials are transition metal dichalcogenides (TMDs),[29] hexagonal boron nitride (hBN),[30] graphitic carbon nitride,[31] 2D black phosphorus,[32] transition metal carbides, nitrides and carbonitrides (MXenes),[33] layered double hydroxides (LDHs),[34] 2D metal oxides/sulphides,[35] 2D metals,[36] 2D polymers,[37] 2D metal–organic frameworks,[38] 2D covalent–organic frameworks[39] and 2D perovskites.[40] Among these 2D nanomaterials, TMDs, hBN and MXenes have been used to synthesize polymer composites,[8,41] particularly epoxy composites.

2.3 Functionalization of the filler: purpose and role

Nanomaterials can be functionalized using two ways: covalent and non-covalent routes. Covalent functionalization routes of graphene and its derivatives involve covalent bond formation between organic compounds and either the C=C bond of pristine graphene or oxygen groups of GO. Noncovalent functionalization aims to control the restacking and agglomeration tendency of graphene and improve its dispersion without interfering with graphene's inherent electronic structure. It involves attaching functional groups to graphene surfaces by interactions like van der Waals, ionic, π–π interactions, *etc.*[53]

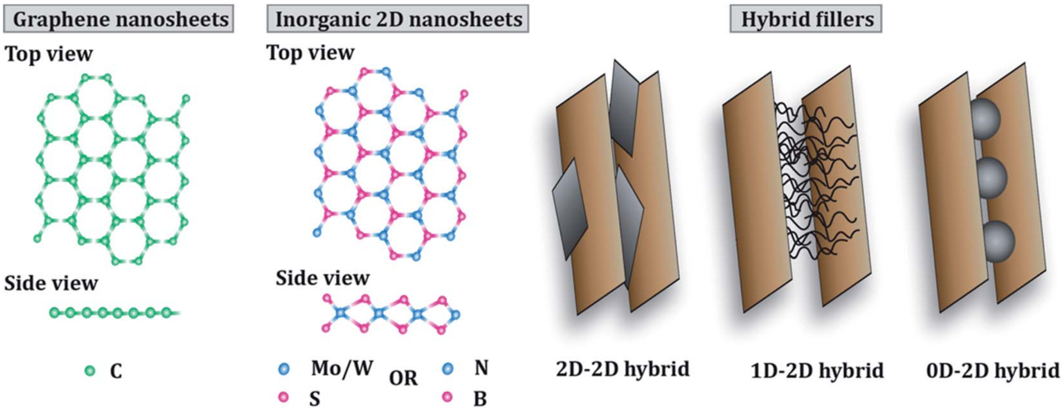

Fig. 1 2D fillers and their multiscale hybrids.

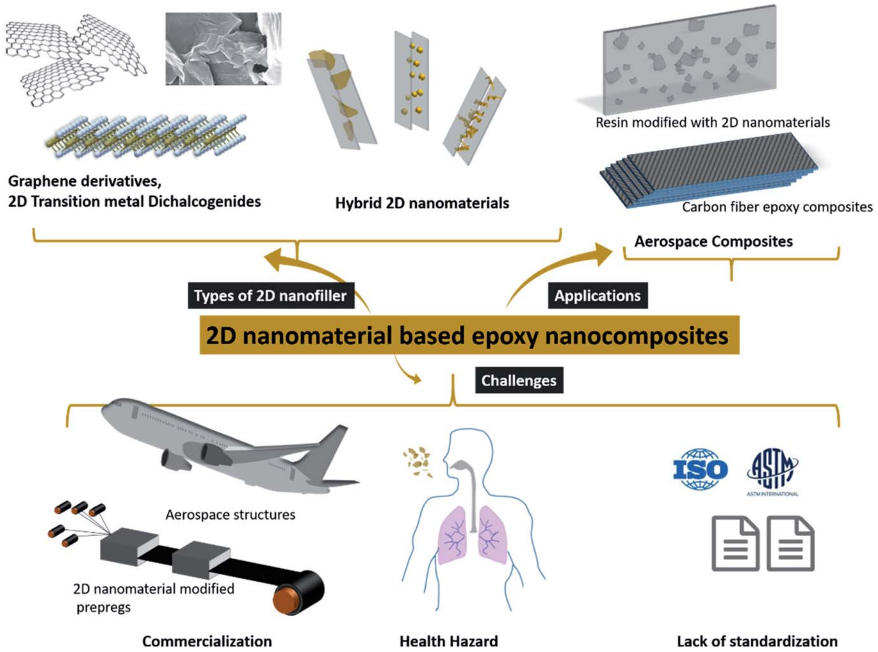

Fig. 2 Types of 2D nanomaterials and applications and challenges of their epoxy-based nanocomposites.

Graphene is hydrophobic and hence disperses in very few solvents. Functionalization improves its compatibility with organic solvents and polymer matrices,[54] which is crucial for the fabrication of nanocomposites. Additionally, these functional groups/compounds can impart new properties to graphene or enhance its inherent properties.

Regarding the epoxy matrix, in particular, functionalized fillers have shown a catalytic effect on the epoxy curing reaction. Functional groups such as amine, carboxyl, hydroxyl, *etc.*, are known to lower the curing activation energy and enhance the cross-linking of the epoxy resin.[55,56] The amine groups, in particular, tend to act as secondary hardening agents, thereby strengthening the epoxy–filler interface.[57–59] The strong filler–matrix interface contributes to improved mechanical properties, as seen in the coming sections.

The uniform dispersion of graphene in the epoxy matrix is challenging due to its large specific surface area and the tendency to restack and agglomerate. The most popular solution for this problem is the surface modification of graphene. Researchers have widely experimented around modifying the surface of graphene with surfactants,[60–62] amines,[63–65] silanes,[66,67] oxygen groups[68,69] and polymers.[70–72] Surface modification of graphene allows the filler to have covalent and non-covalent interactions with the matrix, which helps achieve uniform dispersion. When large polymer groups are attached to the filler's surface, the restacking of graphene sheets is reduced due to the steric hindrance produced by the polymer chains. Graphene has also been used in combination with other nano-fillers such as CNTs,[73–75] rubber,[76,77] inorganic[78,79] and organic nano-particles,[80,81] inorganic 2D materials,[82] *etc.* to make hybrid fillers for epoxy composites. The introduction of organic and inorganic nanoparticles between graphene sheets is known to reduce their restacking tendency, thereby synergistically improving

Table 1 Mechanical properties of nanomaterials

Nanomaterial type	Young's modulus (TPa)	Tensile strength (GPa)	Fracture toughness (MPa m$^{0.5}$)	Ref.
Monolayer graphene	1	130	4–5	9 and 42
Monolayer GO	0.2	28.5 and 35.3 for hydroxyl rich and epoxide rich GO respectively	1.0 and 1.16 for hydroxyl rich and epoxide rich GO respectively	43 and 44
Monolayer rGO	0.25	0.9	2.8–3	45
SWCNTs	1	175	2.7	46 and 47
MWCNTs	0.95	63		48
MoS_2	0.33 (5–25 layers)	23 (monolayer breaking strength)		49 and 50
WS_2	0.27			51
BN	1.16 (t = 15 nm)			52

the filler matrix interaction and contributing towards improved mechanical and thermal properties.

Due to its ease of synthesis and high yield, graphene oxide (rather than graphene) is often used as the base filler material for polymer nanocomposites. The presence of oxygen groups on the surface of GO provides ample opportunity for the surface to be effectively functionalized further using amines or polymers. However, that is not the case with inorganic 2D nano-sheets. In the case of epoxy composites, TMDs functionalized with amines,[83] surfactants,[84] and silanes[85] have been reported. However, compared to functionalized graphene, fewer reports are available on surface functionalized inorganic 2D nanosheets to reinforce epoxy composites.

Yet, surface functionalization of TMDs, inspired by the functionalization routes used for graphene oxide, has been studied by some researchers. Depending on the desired end application, the functionalizing species can be customized, and the surface of the TMDs can be fine-tuned to achieve specific surface interactions. Presolski *et al.*[86] have classified TMD functionalization methods into two categories: thiol/sulphur functionalization[87,88] and nucleophilic reactivity.[89] Covalent functionalization of TMDs is commonly done at defect sites using electron transfer reactions. Surface modified TMDs display increased compatibility with organic solvents. Functionalization of TMDs improves their dispersion and exfoliation and brings about dramatic changes in their inherent mechanical, catalytic, optical and electrical properties.

3. 2D nanosheet filled epoxy composites: fabrication and properties

This section will focus on the effect of 2D nano-sheets on the mechanical properties of epoxy composites. Before the discovery of graphene, several other filler materials were popularly used to reinforce epoxy. These include rubber, core–shell rubber, rigid inorganic nanoparticles, CNTs, *etc.* Table 2 summarizes the advantages and limitations of the various fillers used to synthesize epoxy composites. The several advantages that graphene offered over the other fillers attracted the attention of the research community.

3.1 Graphene epoxy composites

3.1.1 Graphene/rGO epoxy composites. A vast amount of literature is available on epoxy reinforced with graphene and its derivatives. Due to epoxy resin's brittle nature, major emphasis has been made on improving the fracture toughness of epoxy composites. Graphene platelets have been a popular reinforcing agent for epoxy resin for more than a decade. Moreno *et al.*[99] customized thermal reduction cycles of GO to study the effect of thermally reduced GO (TRGO) on the mechanical and electrical

Table 2 Merits and demerits of various types of fillers used to reinforce epoxy

Filler type	Size range	Merits	Demerits	Ref.
Rubber/CSR	Rubber: μm CSR: sub-μm	Large improvement in fracture toughness of epoxy composites	Lower tensile and thermal properties and increased viscosity of composites. No control over the size of rubber because it phase separates during curing. Very high loading (approx. 10–30 vol%)	90–92
Rigid inorganic nanoparticles	Diameter: nano	High inherent thermal stability and modulus. Improved fracture toughness (less than rubber) and tensile properties in epoxy composites	Agglomeration issues. High nanoparticle loading (1–20 vol%) is required to improve the mechanical properties. Processing is difficult due to the increased viscosity of epoxy composites	11, 93 and 94
CNTs	Diameter: nano *L*: μm	High aspect ratio, inherently high tensile properties of CNTs. Low loading (<5 wt%) results in improved mechanical properties in epoxy composites	Unbundling/separating CNTs is challenging. Maintaining the aspect ratio is tough	10, 95 and 96
Graphene and 2D nanofillers	t: nano *L*: μm	Graphene has the best inherent strength and stiffness among nanomaterials. At low loading (0.04 wt%), thermal and mechanical properties both improve in epoxy composites	Dispersion in epoxy is difficult due to restacking, folding, agglomeration issues. Surface modification improves dispersion but creates defects, lowering the inherent strength	9, 97 and 98

properties of epoxy composites. GO was thermally reduced at three different temperatures 700 °C, 1000 °C and 2000 °C. The best mechanical properties were reported for 2 wt% TRGO-700/epoxy composites with 16% higher *E* than the neat resin. More oxygen groups were retained on the surface of TRGO when reduced at 700 °C as compared to 2000 °C, thereby improving filler-matrix interaction. TRGO-2000 contains fewer defects because of the rehybridization of sp^3 C to sp^2 C, to a large extent restoring the graphitic structure. As a result, it is more suitable for electrical applications. Wu *et al.*[100] reinforced a blend of bi-functional epoxy resin using multilayer graphene nano-platelets (GnPs). An external electric field was employed to align the graphene flakes (Fig. 3). At 1.5 wt% loading, the G_{IC} improved by 891% when graphene flakes were aligned perpendicular to the crack propagation direction. An improvement of 681% in G_{IC} was observed for 2 wt% loading, in the case of randomly oriented graphene flakes. The thermal and electrical conductivities also increased substantially. Rafiee *et al.*[101] compared the effect of graphene platelets (GPLs) and CNTs on the mechanical properties of epoxy composites and concluded that GPLs performed better. 0.1 wt% GPL/epoxy composites showed 53%, 31% and 40% improvement in mode I fracture toughness (K_{IC}), Young's modulus (*E*) and ultimate tensile strength (UTS) as compared to neat epoxy, respectively. The superiority of GPLs over CNTs was attributed to the large specific surface area, planar geometry and better interlocking with the epoxy matrix due to the wrinkled morphology of GPLs. Wei *et al.*[102] reported an improvement of 13% in UTS and 30% in storage modulus for 0.3 wt% graphene/epoxy composite.

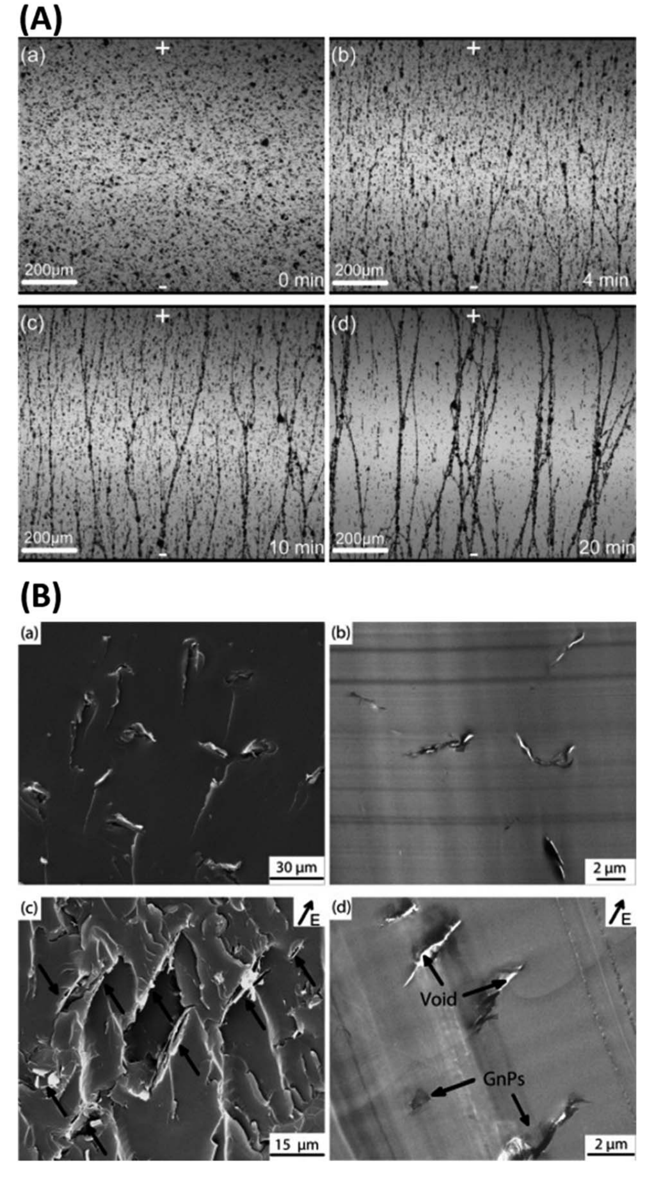

Fig. 3 (A) Optical microscopy images of aligned GnPs in GnP/epoxy composite before (a) and after (b, c and d) applying an electric field; (B) SEM (a and c) and TEM (b and d) images of the epoxy nanocomposites showing randomly oriented and aligned GnPs in epoxy composites.[100] Reprinted with permission from ref. 100 (Copyright © 2015, Elsevier).

Chandrasekaran *et al.*[103] compared the toughening effects of three nanofillers on DGEBA. It was observed that at 0.5 wt% MWCNT, GNP and TRGO loading, epoxy composites displayed 8, 24 and 40% improvement in fracture toughness, respectively. The performance of TRGO was the best due to the increased filler-matrix interaction among the three fillers. Tang *et al.*[104] prepared rGO/epoxy composites using two dispersion techniques, one by solution mixing using acetone and second by employing planetary ball milling. The latter gave rise to a well-dispersed filler, confirmed using TEM and TOM images. For 0.2 wt% well-dispersed rGO loaded epoxy, K_{IC} improved by 52% and glass transition temperature (T_g) increased by 11 degrees compared to neat epoxy.

3.1.2 GO/epoxy composites. As mentioned previously, oxidation of graphite attaches hydroxyl, carboxyl and epoxide groups to the surface of the sheets, facilitates exfoliation and makes them compatible with a range of polar solvents and polymers. As a result, plenty of research has been conducted related to the mechanical and thermal properties of GO/epoxy composites. Yang *et al.*[105] reported remarkable improvement in compressive failure strength and toughness by 48.3 and 1185.2%, respectively, at a mere loading level of 0.0375 wt% GO to the epoxy matrix. The reason behind the improved properties was uniformly dispersed GO because the GO/epoxy composites were prepared by a two-phase extraction process using an aqueous dispersion of GO. Rafiee *et al.*[106] reinforced epoxy with GO prepared from oxidation of graphite flakes. Remarkable improvement of 65%, 115%, 50% and 45% was observed in K_{IC}, G_{IC}, *E* and UTS at a mere 0.125 wt% GO loading as compared to the base resin, respectively. The reported fatigue properties showed a 25 times lower da/dN value for the nanocomposite than the base epoxy. These improvements were attributed to the doubling of surface roughness when GO loading was increased from 0 to 0.125 wt%. On increasing the loading further, the roughness effect appeared to saturate. Bortz *et al.*[107] synthesized graphene by opening helical carbon nanofibers to obtain graphene nanoribbons and further oxidized it to obtain GO. Remarkable tensile strength and modulus of 73.57 MPa and 3.32 GPa at 0.5 and 0.1 wt% GO were reported, respectively. K_{IC} and G_{IC} improved by 62% and 110%, respectively, for 1 wt% GO/epoxy composites as compared to neat epoxy. Flexural modulus and strength improved by 12% and 23%, respectively, at 1 wt% GO loading. Muñoz *et al.*[108] reported 39% and 13% improvement in compressive elastic modulus and flexural modulus, respectively, for 0.3 wt% commercially available GO-loaded epoxy. Xue *et al.*[98] reported an improvement of 10%, 9% and 56% in E, UTS and lap shear strength at 1 wt% GO loading in epoxy, respectively. The T_g also improved by over 4 degrees at 1 wt% GO loading. Kang *et al.*[109] reported 80% and 98% higher impact toughness and K_{IC} at 1 wt% GO loading in epoxy, respectively. A green solvent-free filler dispersion method was adopted by Tang *et al.*,[110] wherein GO was phase transferred from its aqueous dispersion into epoxy resin (E51) using triglycidyl *para*-aminophenol (TGPAP) as the functionalization and phase transfer agent (Fig. 4). This dispersion method is easy to scale up and ensures uniform filler dispersion. A blend of E51 and 20 wt% TGPAP containing 1 wt% GO showed an improvement in the storage modulus, tensile strength and toughness by 43%, 92% and 126% compared to the neat resin, respectively. The flexural strength, modulus and microhardness of the above composite were 37%, 38% and 137%

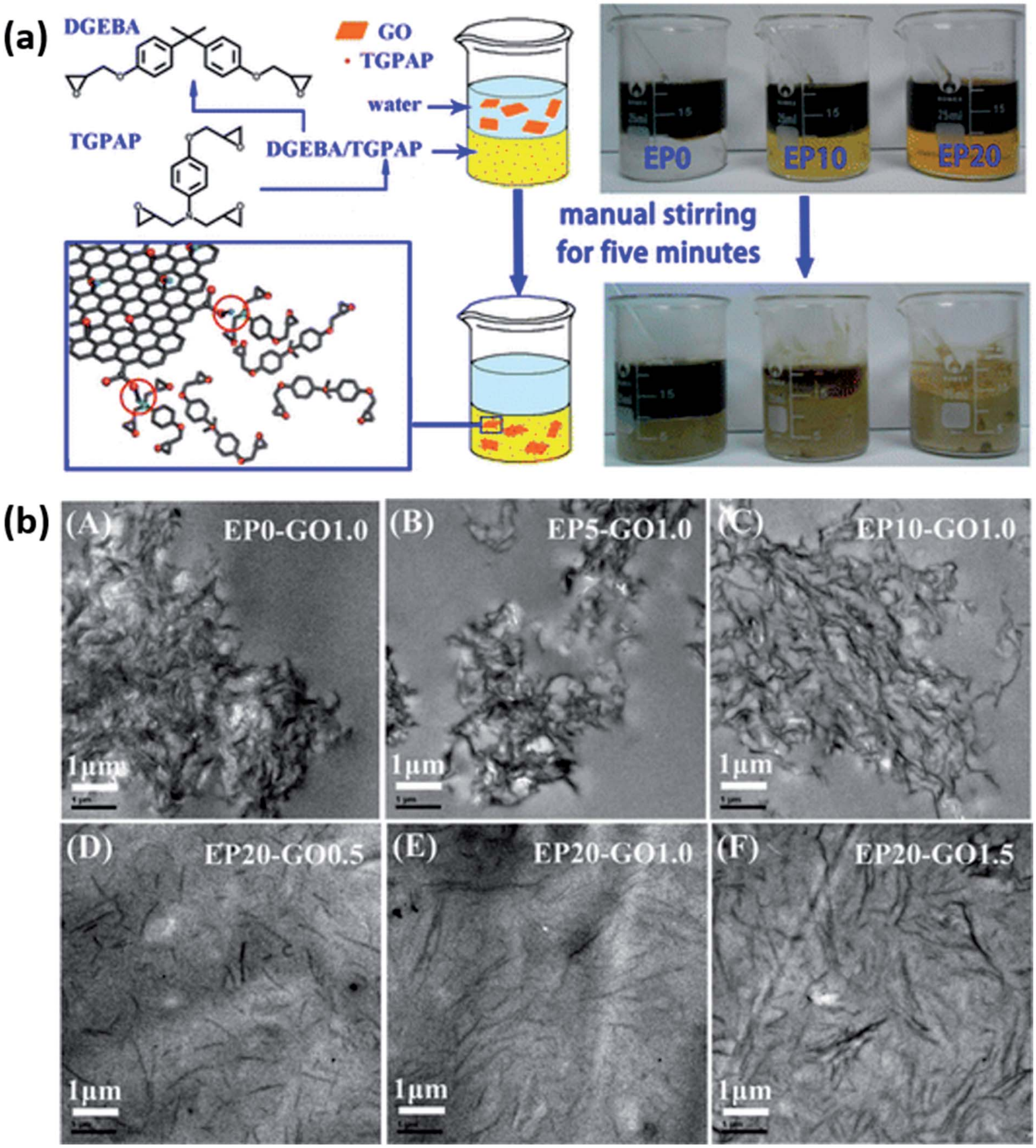

Fig. 4 Schematic and digital images of composites fabricated by the phase transfer method (a); TEM images of nanocomposites at various concentrations of the filler (b).[110] Reprinted with permission from ref. 110 (Copyright © 2016, American Chemical Society).

higher than the neat resin, respectively. Wei *et al.*[69] systematically studied the effect of the extent of oxidation of GO sheets on the mechanical properties of GO/epoxy composites. Various batches of GO were synthesized using the Hummers method by varying the concentration of $KMnO_4$ and reaction time. TEM results confirmed that the best dispersion was observed for the GO 4 batch consisting of the following reactant concentrations: 1 g graphite, 1 g $NaNO_3$, 6 g $KMnO_4$ and 48 ml H_2SO_4 reacted for 6 hours. The 0.2 wt% GO_4/epoxy composite showed 56% and 128% improvement in K_{IC} and G_{IC} compared to the neat resin, respectively. It was concluded that the extent of oxidation of graphene affects the covalent bonding between the GO and epoxy matrix. Hence, an optimal level of oxidation is required to achieve the best filler-matrix interaction and, in turn, the best mechanical properties.

3.1.3 Amine-GO/epoxy composites. Amine functionalized graphene derivatives are a common filler material for epoxy composites. The availability of primary amine groups on the surface of the filler allows it to undergo favorable covalent interactions with the epoxy matrix, thereby strengthening the filler–matrix interface. Ferreira *et al.*[111] used hexamethylene diamine functionalized GO (AGO) to reinforce epoxy. In the case of 1 wt% AGO/epoxy composite 33% and 25% higher hardness and storage modulus were reported as compared to neat epoxy, respectively. Chatterjee *et al.*[65] used dodecyl amine (DDA) functionalized expanded graphene nano-platelets (EGNPs) to reinforce epoxy and reported a 66% higher K_{IC} for 0.1 wt% EGNP/epoxy composites as compared to neat epoxy. Flexural modulus increased by 15% at 2 wt% loading due to improved load transfer (Fig. 5). Ashori *et al.*[112] used GO functionalized with three different amines: ethylenediamine (EDA), 4,4′-diamino diphenyl sulfone (DDS) and *p*-phenylenediamine (PPD) as a filler for carbon fiber reinforced epoxy. The evaluation of fracture surface morphology indicated that the interfacial interaction was strengthened due to the introduction of functional groups on the surface of GO. Fang *et al.*[113] reported 60% and 53% improvement in E and UTS of 0.4 wt% methylene dianiline (MDA) modified rGO/epoxy composites, respectively. The fracture toughness and flexural strength improved by 94% and 92% for 0.6 wt% filler loading, respectively. Seong *et al.*[114] reported 120% and 63% improvement in impact toughness and storage modulus in 1.5 phr MDA modified GNP/epoxy composites compared to 86% and 39% improvement in 1.5 phr GNP/epoxy composites, respectively. Naebe *et al.*[115] compared the reinforcing effects of thermally reduced GO (TRG), and TRG modified with the Bingel reaction (FG) on epoxy composites. It was reported that 0.1 wt% TRG and FG/epoxy composites show 15% and 22% higher flexural strength and

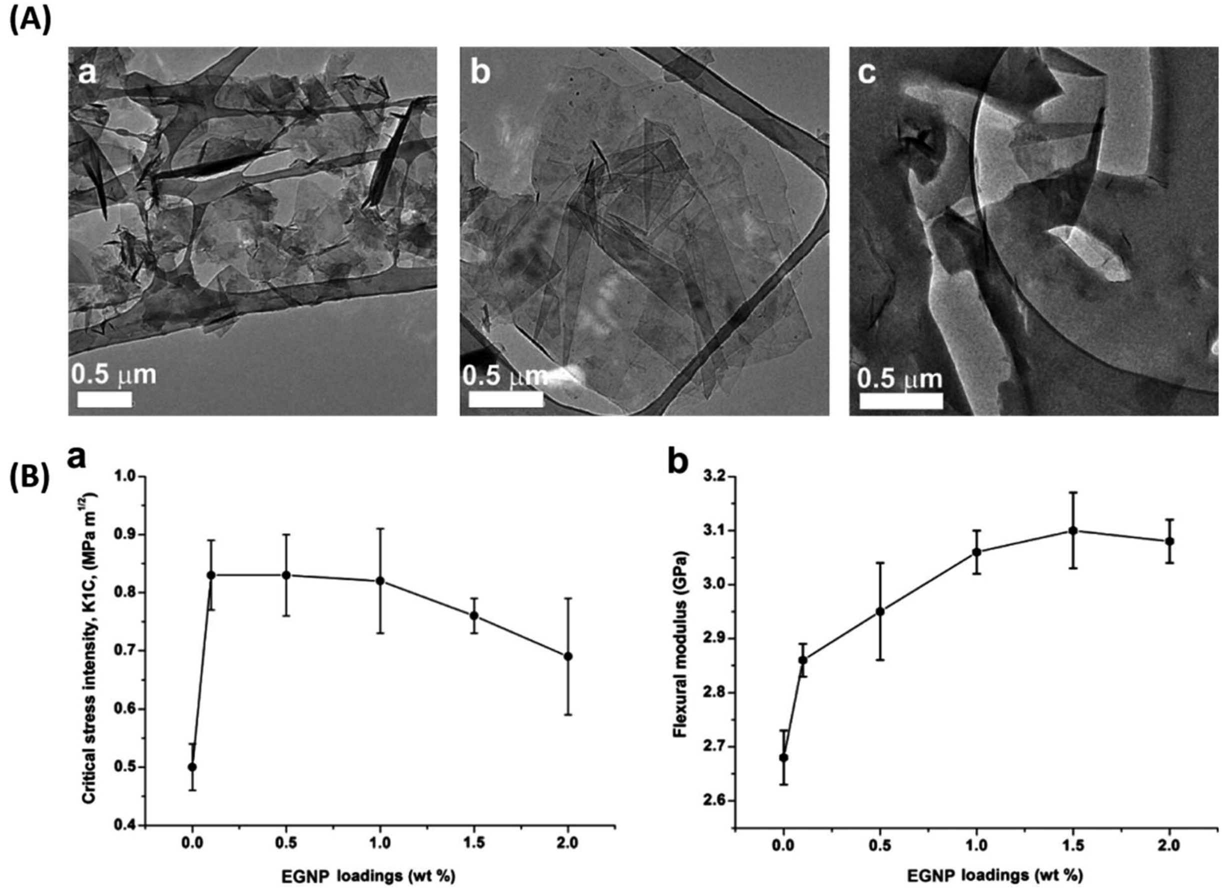

Fig. 5 (A) TEM images of amine-EGNPs (a and b) and 0.5 wt% amine-EGNP/epoxy composite (c). (B) Mechanical properties of epoxy composites with different EGNP loadings.[65] Reprinted with permission from ref. 65 (Copyright © 2012 Elsevier B.V.).

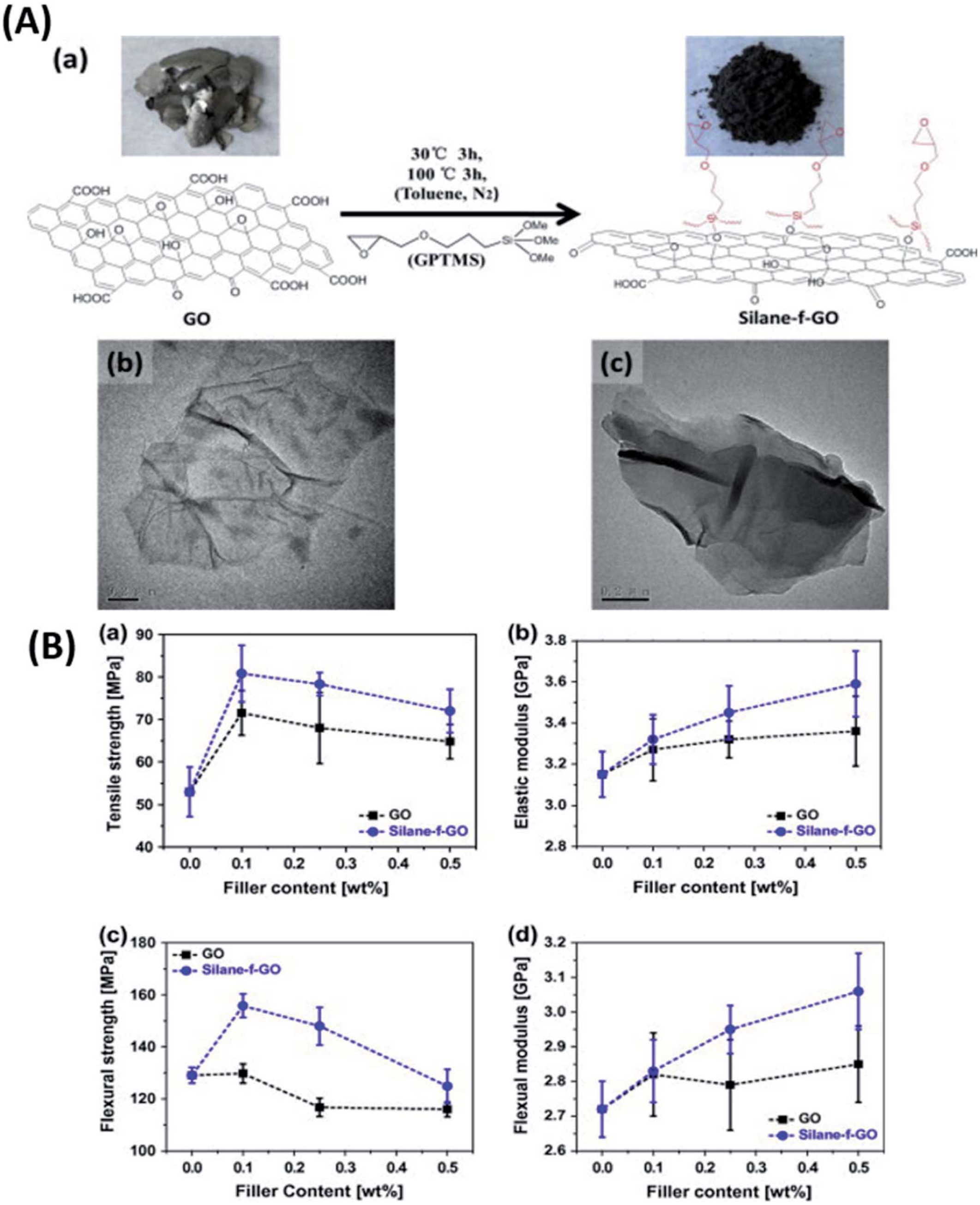

Fig. 6 (A) Synthesis route schematic of silane functionalized GO (a) and TEM images of GO (b) and silane-f-GO (c) and (B) mechanical properties of epoxy nanocomposites (a–d).[66] Reprinted with permission from ref. 66 (Copyright © 2014 Elsevier Ltd).

6% and 16% higher storage modulus than neat epoxy, respectively. Guo *et al.*[116] reported that GO modified with triazine derivatives (GO–TCT–DETA) dispersed more uniformly in epoxy matrix whereas blank GO agglomerated. A 49% and 15% higher flexural strength and modulus was reported for 0.1 wt% GO–TCT–DETA/epoxy composite as compared to neat epoxy, respectively.

3.1.4 Silane-GO/epoxy composites.

Many authors have reported promising results for epoxy reinforced with silane-modified graphene derivatives[117] to enhance the corrosion resistance,[118,119] mechanical and thermal properties of epoxy composites. Wan *et al.*[66] reported that superior dispersion of silane-f-GO in the epoxy matrix was achieved compared to GO. Fig. 6A shows a schematic of GO functionalization using glycidoxypropyltrimethoxy silane (GPTMS). The TEM image of silane-f-GO appeared darker than that of GO indicating attachment of functional groups to the surface of GO. The storage modulus increased by 52% for 0.5 wt% silane-f-GO/epoxy composite indicating that the silane groups improved the filler matrix interaction and increased the stiffness of epoxy (Fig. 6B). The tensile and fracture properties also improved. Li *et al.*[120] compared the tensile and fracture properties of epoxy

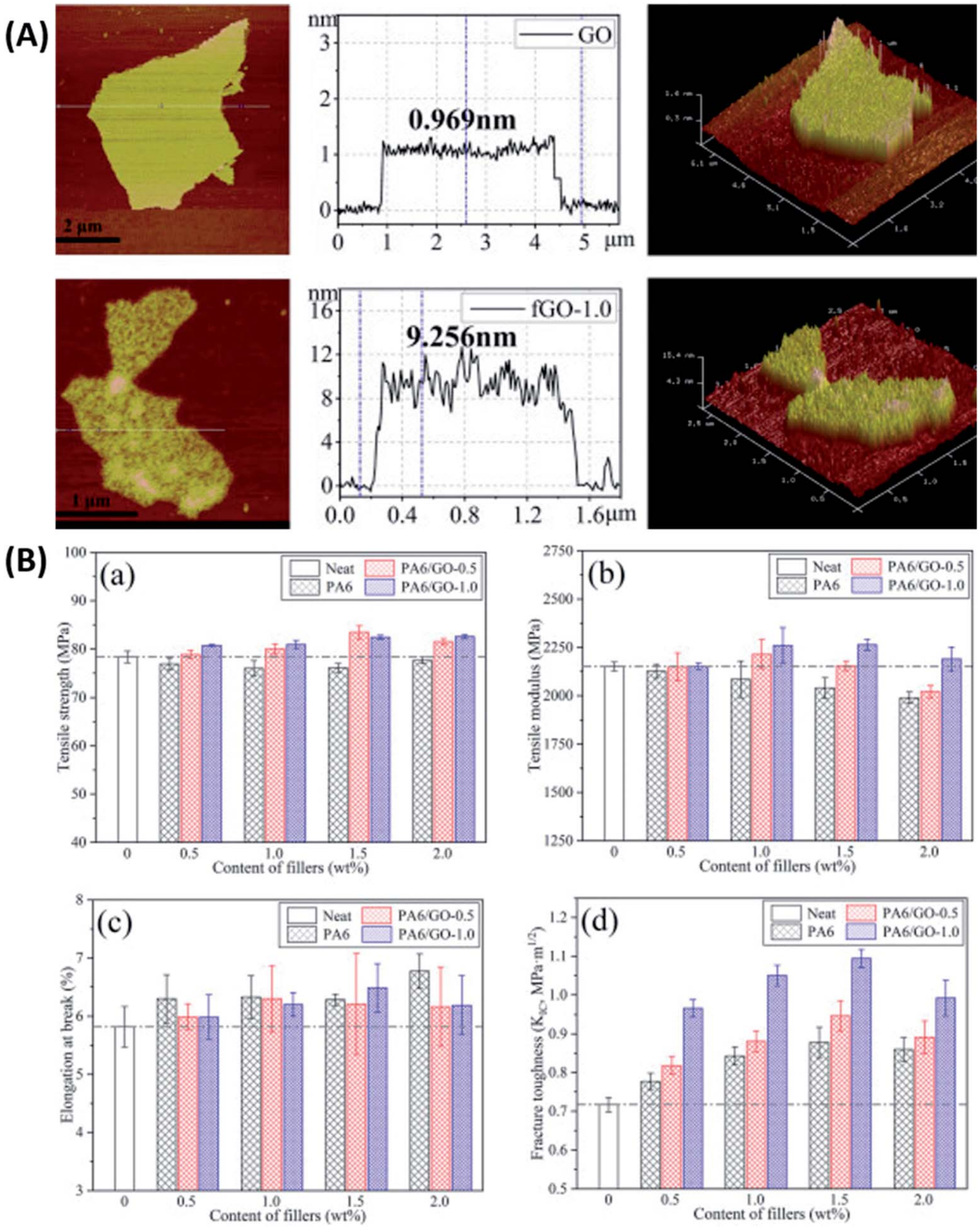

Fig. 7 (A) AFM images and sheet thickness analysis of GO (a) and PA6–GO (b) and (B) tensile (a–c) and fracture (d) properties of epoxy composite.[128] Reprinted with permission from ref. 128 (Copyright © 2018 Elsevier Ltd).

reinforced with amino-silane functionalized GO (APTS-GO), and epoxy-silane functionalized GO (GPTS-GO). The authors concluded that GPTS-GO was more uniformly dispersed than APTS-GO, but the latter offered better interfacial stress transfer. Hence, depending on the silane groups attached to GO, the properties of the final epoxy composites can be customized. Moghadam *et al.*[121] reported that 0.5 wt% G–Si/epoxy composites showed 38% and 14% improvement in UTS and E, respectively. K_{IC} increased by 86% for 0.5 wt% G–Si/epoxy composites as compared to neat epoxy.

3.1.5 Polymer-*g*-GO/epoxy composites. In comparison to the other covalent functionalization methods of graphene, surface modification using polymer chains is promising because it is cost-effective and efficient.[122,123] Wan *et al.*[70] successfully reinforced diglycidyl ether of bisphenol-A (DGEBA) resin with DGEBA grafted GO and reported enhanced tensile and fracture properties. The use of the matrix as a functionalizing species enhanced the filler dispersion and filler matrix interaction. Similar studies were reported by Zhao *et al.*[124] Recently, researchers[71,125] studied the effect of hyperbranched polyamide (HBPA) functionalized GO on epoxy composites. Li *et al.*[71] used amine-terminated HBPA instead of blank HBPA to functionalize GO. Due to the amine groups on HBPA, Li *et al.* reported improvement in tensile properties at a mere 0.15 wt% loading compared to 0.5 wt% HBPA loading in the case of Qi *et al.*[125] Apart from the tensile and thermomechanical

Table 3 Percentage improvement in UTS, E and K_{IC} of graphene epoxy composites

	Filler							
Resin and hardener	Name	Size	Loading	Dispersion method	UTS (%)	E (%)	K_{IC} (%)	Ref./year
DGEBA and DETDA 100 : 24.4	GO-*g*-PEG		0.1 wt%	Acetone, sonication			334	2020 (ref. 131)
E44 and DDS (26 : 7.8)	Polycaprolactone–graphene		1 wt%	Acetone, sonication	87			2020 (ref. 132)
DGEBA and DETDA 100 : 24.4	GO		0.5 wt%	Acetone, sonication	25		90	2020 (ref. 133)
	GO–TBCP	Miscelle dia = 6–11 nm	0.5 wt%		32		397	
DGEBA and aliphatic amine	PA6/GO	$t = 9.25$ nm	1.5 wt%	Filler added to the hardener, sonication		5	53	2019 (ref. 128)
E51 DGEBA and hardener	GO-2021P	$t = 8.33$ nm	1 wt%	TRM	34	26		2019 (ref. 134)
DGEBA and DDM	Acid treated graphene	$t = 1$ nm	0.2 wt%	Ethanol, sonication	14			2019 (ref. 135)
Araldite MY 721 and Aradur 9664	GO-*g*-PAA		0.7 wt%	Ethanol, sonication			87	2019 (ref. 72)
Epoxy E 51 and DDM H-256	GO		0.1 wt%	Acetone, sonication	27	14		2019 (ref. 130)
	GO–TCT–Tris		0.1 wt%		41	28		
E51 and D230 in the ratio 100/30	HBPA–GO	3–5 layers	0.15 wt%	Filler added to the hardener, sonication	42			2019 (ref. 71)
DGEBA E44 and DDS	GOFO		0.5 wt%	THF by sonication	20	12		2019 (ref. 136)
Epoxy 5417A 2 : 1	GO		0.2 wt%	Filler added to the hardener, sonication	16	6	56	2018 (ref. 69)
DGEBA WSR618 and QS-1622 (2 : 1)	HBPA–GO		0.5 wt%	THF by sonication	23	18	44	2018 (ref. 125)
YD-128 and hardener	GNP	$L = 10$ μm	2 wt%	Acetone, sonication	6	66		2018 (ref. 137)
	Melamine fGNP	$L = 10$ μm	2 wt%		34	95		
Araldite LY 1564 and Aradur 3487 1 : 0.34	GO		0.25 wt%	Filler added to the hardener, sonication	15	13		2018 (ref. 68)
DGEBA E51 and H-256 hardener	GO	$L =$ few μm	0.1 wt%	Acetone, sonication	26	15		2018 (ref. 116)
	GO–TCT–DETA		0.1 wt%		41	28		
Lapox-B-11 and Lapox AH-713 2 : 1	TZG		0.1 wt%	DMF, sonication	32	35	133	2018 (ref. 138)
DER 354 and DETDA	DG	$t = 1.2$ nm $L = 1$ μm	0.8 wt%	Acetone, sonication	37			2017 (ref. 139)
RL 440 and t HY 441 in 100 : 20	Ppy–GO		1.5 wt%	Acetone, sonication	51	84		2017 (ref. 140)
EPOLAM 2063 and hardener 100/107	GO		0.5 wt%	Ethanol, sonication	3		19	2017 (ref. 141)
	HPEEK–GO		0.5 wt%		7		31	
YD128 and DDM	GO	$L = 0.25$–5 μm, $t = 0.927$ nm	1 wt%	Acetone, sonication			98	2017 (ref. 109)
NPEL-128S and F205 in 100 : 58	GO–ODA		0.5 wt%	Acetone, sonication	104	97		2017 (ref. 142)

Table 3 (*Contd.*)

	Filler							
Resin and hardener	Name	Size	Loading	Dispersion method	UTS (%)	E (%)	K_{IC} (%)	Ref./year
Araldite LY 564 and Aradur 2954 100/35	Plasma-fGNP	$L = 1–3$ μm	0.25 wt%	Methanol, sonication	2	5	22	2017 (ref. 143)
YD128	GO		0.4 wt%	Acetone, sonication	168	104		2017 (ref. 144)
Epofix resin and hardener 25 : 3	G-EP	$t = 2.2$ nm	1 wt%	DMF, sonication	116	96		2016 (ref. 124)
DGEBA YD-128 and DDS 100 : 21	DDS–GO	$t = 1$ nm, $L =$ 100–500 nm	0.1 wt%	Filler acted as a co-curing agent	26			2016 (ref. 63)
LY5052 and HY5052 (100/38)	DC-GR	$t = 2.13$ nm	0.2 wt%	Acetone, sonication	56	26		2016 (ref. 145)
DGEBA/MHHPA (180/175)	TRGO		0.2 wt%	Ethanol, planetary milling			52	2015 (ref. 61)
	Triton-TRGO		0.2 wt%		52		65	
Epon 828 and hardener (100 : 14.5)	ATBN-GNP	$L = 5$ μm, $t <$ 10 nm	5 wt%	Acetone, sonication			93	2015 (ref. 146)
E51 and TGPAP blend	GO		1.5 wt%	Phase transfer method	92			2015 (ref. 110)
DER-331 and DEH 24 (100/15)	GO–TEPA	$t = 1.5$ nm	0.5 wt%	TRM		72		2015 (ref. 64)
Araldite F and DDM	M25 graphene	$L = 25$ μm, $t = 6$ nm	5 wt%	Filler added to resin, sonicated		28		2015 (ref. 147)
E-44 and DDS (3.33)	PBI–HPG–RGO	$t = 16$ nm	0.7 wt%	Acetone, sonication	62			2015 (ref. 129)
DGEBA/MHHPA in 180/175	Silane fGO	$L = 1–3$ μm	0.1 wt%	Acetone, planetary milling			39	2014 (ref. 66)
			0.25 wt%		48	10		
Epon 828 and D230	ATBN–GO		0.04 wt%	Filler added to the hardener, sonication,			50	2014 (ref. 97)
DGEBA/MHHPA in 180/175	GO	$L =$ few μm	0.5 wt%	Acetone, sonication, planetary milling	22			2014 (ref. 127)
	D 230-f-GO		0.5 wt%		63	12		
	D 2000-f-GO		0.5 wt%		51	10		
Araldite GY 191 and HY 956	GO with CF	$L = 2$ μm	0.1 wt%	Acetone, sonication		27	54	2014 (ref. 148)
Araldite LY556 and Aradur 917 100/90.1	GNP	$t = 12–15$ nm $L = 20–50$ μm	1.0 wt%	TRM			43	2014 (ref. 103)
DGEBA/MHHPA 180/175	GO	$t = 0.486$ nm	0.25 wt%	Acetone, sonication, ball milling	28	5	26	2014 (ref. 70)
	DGEBA-*g*-GO	$t = 0.865$ nm	0.25 wt%		75	13	41	
KEM 101 and KH 700 in 5 : 1	*In situ* rGO	Area: 176.4 μm^2	1.5 wt%	Aqueous phase transfer	500	70		2013 (ref. 149)
DGEBA and MHHPA	rGO	$t = 1.23$ nm	0.2 wt%	Ethanol, sonication, ball milling			52	2013 (ref. 104)
LY5052 and HY5052 (100 : 38)	APTS-GO		0.2 wt%	Acetone, sonication	16	32		2013 (ref. 120)
	GPTS-GO		0.2 wt%				72	
DGEBA and hardener	APTS-rGO	$t = 2.696$ nm	1 wt%	Acetone, sonication	45			2012 (ref. 67)
Epikote Epikure 100/24	DDA–graphene		0.1 wt%	Acetone, TRM			66	2012 (ref. 65)
DGEBA and MDA (100/27)	AB-graphite	2–15 layers	4 wt%	Ethanol, sonication	30	40		2011 (ref. 150)
Resoltech 180/1805	GO	$L = 2$ μm	0.5 wt%	Acetone/TRM	13	5	63	2011 (ref. 107)
Epoxy 2000 and 2120 epoxy	FGS	$t = 2–3$ layers	0.125 wt%	Acetone, sonication	45	50	65	2010 (ref. 106)
Epon 828	MDA–GO	$t = 4.83$ nm	0.6 wt%	Acetone, sonication	53	60	94	2010 (ref. 113)

properties, flexural strength and modulus increased by 43% and 97% for 0.15 wt% GO–HBPA–NH_2 loading in epoxy respectively.[71]

In another recent study, Mi *et al.*[126] modified GO with hyperbranched polyamide (HPA). Impact strength, tensile strength, flexural strength and flexural modulus for 0.10 wt% HPA–GO/epoxy composite increased by 310%, 37%, 8% and 10% compared to neat epoxy, respectively. The interfacial properties of the filler were quantified using contact angle measurements. Interestingly, it was reported that after HPA grafting, the water contact angle of GO increased, making it hydrophobic, but its DGEBA contact angle reduced, lowering the interfacial energy. Guan *et al.*[127] used two types of polyetheramine with different chain lengths (D230 and D2000) to modify the surface of GO. The UTS improved by 63% and 51%, *E* by 12% and 10% and tensile toughness by 90% and 119% for 0.5 wt% D230-*g*-GO and D2000-*g*-GO/epoxy composites, respectively. The authors proved that the interphase between

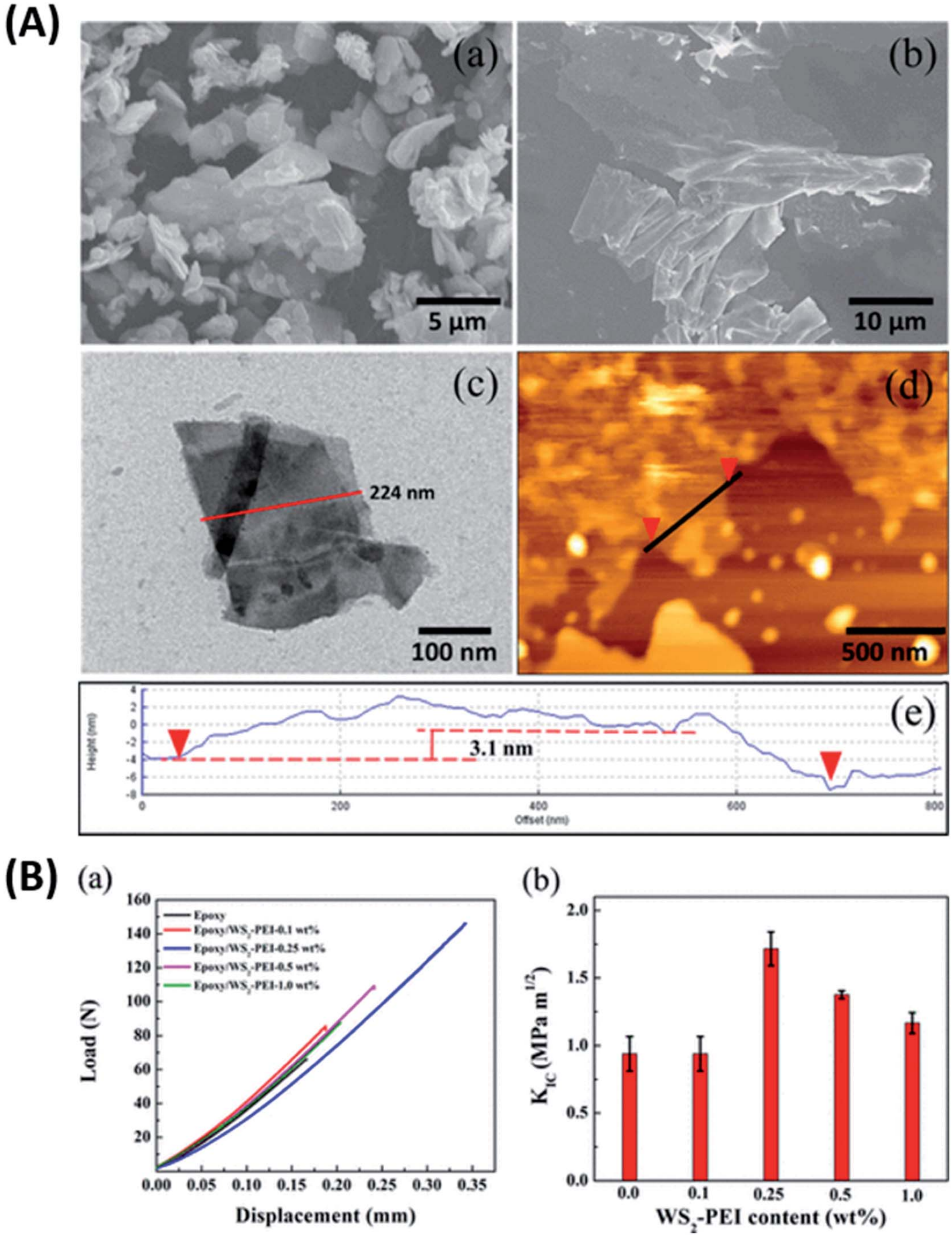

Fig. 8 (A) SEM images of bulk WS_2 (a). SEM (b), TEM (c) and AFM (d and e) images of PEI functionalized WS_2 and (B) fracture toughness of the PEI–WS_2/epoxy composites (a and b).[8] Reprinted with permission from ref. 8 (Copyright © 2017, American Chemical Society).

the filler and the matrix could be tuned by grafting polymer chains of different lengths on the surface of GO. Zhao *et al.*[128] reported a method of *in situ* polymerization to graft polyamide 6 (PA6) chains on GO surface. The thickness of GO was observed to increase substantially after functionalization. As a result of functionalization, the surface of PA6–GO appeared rougher than that of GO due to the introduction of defects (Fig. 7A). The author reported 53% higher K_{IC} for 1.5 wt% GO–PA6/epoxy composite as compared to the neat resin (Fig. 7B). The PA6–GO filler contained 1 wt% GO, hence it's noteworthy that the 1.5 wt% GO–PA6/epoxy composite contained only 0.015 wt% GO. Pan *et al.*[129] used perylene bisimide (PBI) as a foundation for oligomerization of glycidol to prepare hyperbranched glycidol (HPG). This polymer, then mounted on rGO, was further used to synthesize epoxy composites. UTS, impact strength and impact toughness increased by 62%, 51% and 148% for 0.7 wt% PBI–HPG–rGO/epoxy composite as compared to the neat resin, respectively. Ma *et al.*[130] modified GO using hydroxyl-terminated triazine derivatives (GO–TCT–Tris). Flexural strength and modulus increased by 49% and 16% for 0.1 wt% GO–TCT–Tris/epoxy composite than the neat resin, respectively. Table 3 summarizes the mechanical properties of epoxy composites reinforced with graphene and its derivatives.

3.2 Inorganic 2D nanosheets/epoxy composites

Graphene is known to impart electrical conductivity to insulating polymers and hence is useful to fabricate electrically conductive polymers. In contrast, TMDs are high bandgap semiconductors and hence incapable of imparting electrical conductivity to polymers. As a result, they are useful in synthesizing epoxy composites with enhanced mechanical

Table 4 Percentage improvement in UTS, E and K_{IC} for epoxy reinforced with inorganic 2D nanofillers

	Filler							
Resin and hardener	Name	Size	Loading	Dispersion method	UTS (%)	E (%)	K_{IC} (%)	Ref./year
W52 and JH93 100 : 25	APTES–BNNS	$t = 2$–3 nm	10 wt%	Hot pressing	2			2020 (ref. 7)
EP (m(EPON828)/m(PPGDGE) = 60/40) and D230	G–MoS_2		1 wt%	Acetone, sonication	500			2019 (ref. 152)
DGEBF NPEF-170 and DMDC	KH580-f-MoS_2	$t = 1$–6 nm	0.7 wt%	THF sonication, TRM	8	22		2018 (ref. 85)
DGEBA Lapox-B-11 and TETA Lapox AH-713 (2 : 1)	CTAB–MoS_2		0.2 wt%	THF, sonication	23	27		2018 (ref. 84)
EP(m(EPON828)/m(PPGDGE) = 55/45) resin and D230	Melamine–MoS_2		0.8 wt%	Acetone, sonication	400	450		2018 (ref. 159)
TGDDMM and DDS	WS_2–PEI	$L = 260 \pm 45$ nm, $t = 3$ nm	0.25 wt%	Ethanol, sonication			83	2017 (ref. 8)
E51 and Jeffamine D230	AT–hBN	$t = 3$–4 nm	1 wt%	THF, sonication	6	5		2016 (ref. 160)
Epon 862 and Epikure hardener	MNP	$t = 5$–10 nm, $L = 400$–500 nm	0.2 wt%	Sonication in 1-vinyl-2 pyrrolidone	32		60	2014 (ref. 151)
Epon 862 and hardener	PBA–BNNF	$L = 200$–500 nm, $t < 7$ nm	0.3 wt%	Acetone, sonication	54	21		2013 (ref. 156)

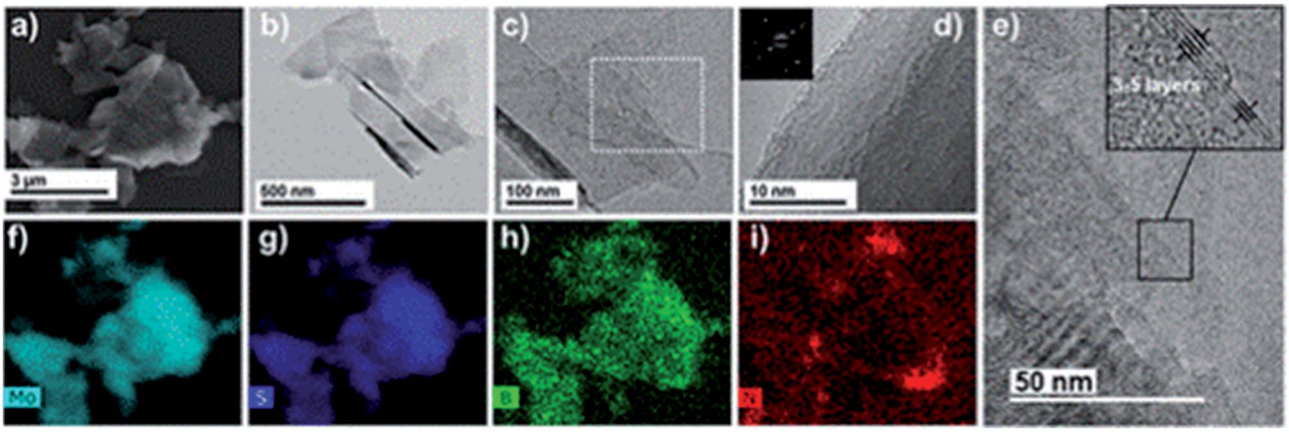

Fig. 9 SEM image (a) and EDS elemental maps of Mo, S, B and N (f–i), TEM and HRTEM images of the MoS_2/h-BN hybrid (b–e).[166] Reprinted with permission from ref. 166 (Copyright © 2019, American Chemical Society).

properties while maintaining the polymer's electrically insulating nature.

Eksik *et al.*[151] used unmodified MoS_2 nanoplatelets (MNPs) to reinforce epoxy and reported improvement in tensile and fracture properties. An improvement of 32%, 60% and 160% was reported in UTS, K_{IC} and G_{IC} of 0.2 wt% MNP/epoxy composite over neat epoxy, respectively. A significant improvement of 13 degrees was observed in the T_g of the same composite compared to the neat resin. Since the author used unmodified MNPs, agglomeration was observed at very low wt% (0.3 wt%) in comparison to the surface-modified fillers. Zhao *et al.*[85] reported a 66% improvement in impact intensity at 0.7 wt% loading of silane-modified boron nitride in the epoxy matrix. An 80% improvement was reported in the apparent shear strength at 120 °C for the same composite. In another study[152] the author has established a relationship between the degree of exfoliation of MoS_2 and its influence on the mechanical properties of epoxy composites. The degree of exfoliation was controlled using the intercalation time. It was reported that the well-exfoliated sheets led to an enormous 500% and 6800% increase in the UTS and E of 1 wt% MoS_2/epoxy composite, respectively. Sahu *et al.*[8] reported a 43% and 65% improvement in compressive and flexural strength for epoxy reinforced with 0.25 wt% PEI modified WS_2. Fig. 8A brings out the difference between the bulk and exfoliated WS_2 sheets. The functionalization of WS_2 nanosheets improved the filler's load transfer ability and led to an 83% improvement in fracture toughness of epoxy-containing 0.25 wt% filler (Fig. 8B).

Boron nitride displays excellent thermal conductivity and has been widely used to fabricate thermally conducting epoxy composites.[153–155] Some researchers have also used hBN to enhance the mechanical properties of epoxy resin. Liu *et al.*[7] reinforced epoxy with (3-aminopropyl)triethoxysilane (APTES) modified boron nitride and reported a 100% increase in tensile strength at 10 wt% loading. T_g increased by 14 degrees for 40 wt% loading. Lee *et al.*[156] compared the reinforcing effects of rGO, and 1-pyrenebutyric acid (PBA) functionalized BNNF (boron nitride nano-flakes). Lee *et al.*[156] showed the filler's TEM image and the statistical analysis of the thickness of BNNFs.

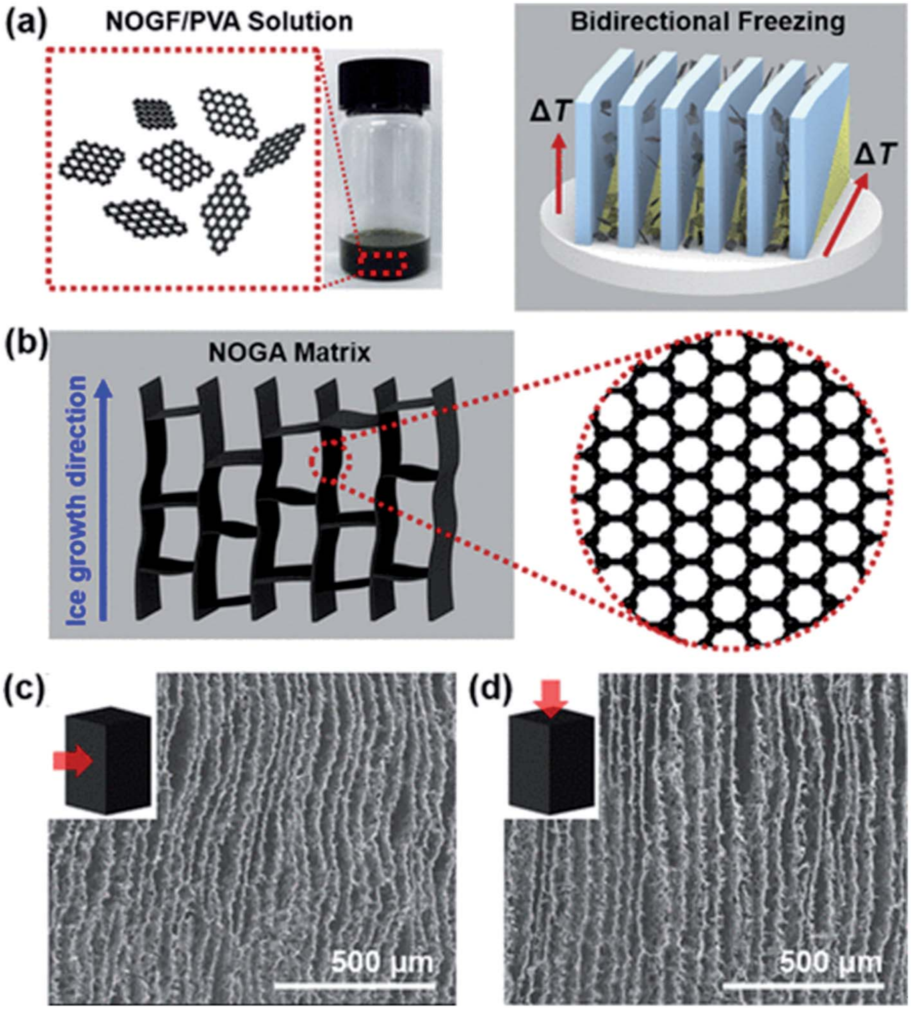

Fig. 10 Schematic of the synthesis of aerographene by bidirectional freezing (a), aerographene structure (b) and aerographene SEM images (c and d).[176] Reprinted with permission from ref. 176 (Copyright © 2018, American Chemical Society).

The author reported that PBA–BNNF performed much better and reported an improvement of 21%, 54% and 107% in E, UTS and tensile toughness of 0.3 wt% PBA–BNNF/epoxy composites, respectively.

Another class of 2D materials called the MXenes has recently gained popularity as a reinforcement material in epoxy composites.[157] Research related to MXene reinforced epoxy is still at a nascent stage. Zhang *et al.*[158] reported a 76% and 66% increase in impact strength and flexural strength for 1 wt% Ti_2CT_x/epoxy composites, but the hardness dropped. The T_g increased by 20 degrees at 2 wt% loading, with a reduction in creep strain. Table 4 gives a summary of epoxy composites containing inorganic 2D nano-sheets as fillers.

3.3 Hybrid filler/epoxy composites

Hybrid fillers are multiscale fillers used to reinforce polymer matrix materials. The major advantage of hybrid fillers is that each individual filler's inherent properties are exploited synergistically to achieve the desired mechanical properties in the final composite. Apart from enhancing electrical,[161,162] thermal[163] and corrosion resistance[164,165] properties, hybrid fillers also provide unique architecture that is capable of strengthening the filler matrix interface and contribute significantly to the mechanical properties of epoxy composites.

3.3.1 2D–2D hybrids. Domun *et al.*[74] reported a 41% and 92% improvement in K_{IC} and G_{IC} on the addition of f-GNP (0.25 wt%)/BNNS (boron nitride nanosheets 0.1 wt%) hybrid to the epoxy matrix, respectively. A hybrid MoS_2/hBN (1 : 1) filler (Fig. 9A) was used in ref. 166 to reinforce epoxy. A 95% higher UTS and 58% higher E were reported for 1 wt% and 0.25 wt% MoS_2/hBN epoxy composite, respectively. The cross-linking density was shown to improve by 45% over the neat resin after the hybrid filler was added to epoxy. This was clear evidence of an improved filler matrix interaction.

3.4 Emerging material derived from graphene: aerographene

Aerogels are 3-dimensional porous and interconnected architecture having an ultralow density, superelasticity,[167] high specific surface area, high adsorption capacity[168] and tunable porosity.[169] Graphene and its derivatives can be used as building blocks to make such 3D structures. Graphene aerogels, also commonly known as aerographene, are widely used in polymer composites to enhance the thermal,[170,171] electrical,[172,173] tribological[174,175] and mechanical properties of the polymer. For example, Kim *et al.*[176] reported a maximum improvement of 76% in the fracture toughness of non-oxidized graphite aerogel (NOGA)/epoxy composite at a loading level of 0.45 vol% as compared to neat epoxy. NOGA was synthesized using a bi-directional freezing process to achieve a robust wall of aligned graphene sheets (Fig. 10). Maximum improvement was achieved when the crack propagation direction was perpendicular to the graphene flake wall alignment. A summary of the mechanical properties of aerographene reinforced composites has been provided in the table below (Table 5).

4. Toughening mechanisms

The toughening mechanisms occurring in the composites can be divided into intrinsic and extrinsic.[184] The toughening mechanisms induced due to the addition of the nano-filler, such as crack deflection, pull out, delamination *etc.*, are extrinsic toughening mechanisms. In contrast, the matrix itself is capable of causing toughening to some extent by undergoing localized plastic deformation, micro-cracking *etc.* These mechanisms fall into the intrinsic toughening category. Fig. 11 represents toughening mechanisms in epoxy reinforced with 2D fillers. Depending on the filler added, the predominant toughening mechanisms vary. To date, a number of fillers have been explored for reinforcing epoxy with a focus on enhancing its fracture properties.

Table 5 Percentage improvement in UTS, K_{IC} and flexural modulus for epoxy reinforced with aerographene

	Filler							
Resin	Type	Synthesis	Loading	Composite fabrication	UTS (%)	K_{IC} (%)	Flex mod. (%)	Ref./year
ML-523 and HA-11	3D nitrogen doped graphene	GO + dicyanamide hydrothermal reduction	0.1 wt%	Ultrasonic mixing	19			2020 (ref. 177)
LY 1556 and XB 3471 100 : 12	Ultra large-GA	Directional freeze drying of GO	0.11 vol%	Vacuum infiltration		69		2018 (ref. 178)
	Small-GA		0.16 vol%			33		
Epoxy and hardener	Multilayer graphene web	CVD on Ni template	8.3 wt%	Vacuum infiltration		100		2018 (ref. 179)
LY1556 and TETA in 100 : 12	Non-oxidized graphene aerogel	Bi-directional freeze casting in PVA	0.45 vol%	Vacuum infiltration		76		2018 (ref. 176)
			0.34 vol%				25	
Aeromarine 300/21	Commercial GF		0.13 wt%	Mold casting	12			2017 (ref. 180)
Rim 135 and Rim 137 100 : 30	Aero-graphite	CVD on ZnO template	0.45 wt%	Vacuum infiltration		19		2016 (ref. 181)
Epoxy and hardener	GA	Reduction using HI, freeze drying	1.4 wt%	Vacuum infiltration		64		2015 (ref. 182)
			0.5 wt%				12	
LY1556 and TETA 100 : 12	GF	CVD on Ni template	0.1 wt%	Vacuum infiltration		70		2014 (ref. 183)
			0.2 wt%				53	

The filler's inherent properties, such as high modulus, breaking strength, fracture toughness, *etc.*, also play a major role in contributing towards a toughened matrix. Graphene and TMDs both display exceptional mechanical strength, which reflects in their epoxy composites. The filler size can affect the extent of toughening. Studies showed that the larger the GO sheet, the more the wrinkles and the more defects associated with the GO sheets. These defects act as stress concentrators and hence lower the fracture toughness. In contrast, smaller sheets have fewer defects and can provide better load transfer and reinforcing capability.[185] Apart from the filler size, filler alignment also plays a role. As compared to random and parallel arrangement, graphene nanoplatelets transversely aligned to the crack growth contribute towards toughening due to increased interaction of the crack with the filler, eventually causing graphene pull-out.[100]

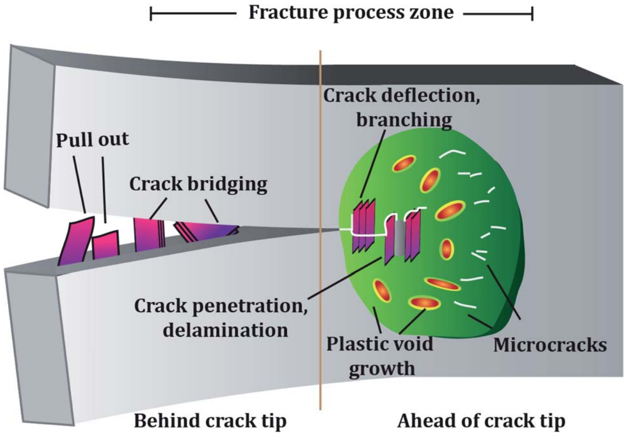

Fig. 11 Toughening mechanisms in epoxy composites reinforced with 2D nanomaterials.

The major toughening mechanisms that underplay in graphene–epoxy composites are crack deflection,[71,186] crack pinning,[71,72] micro-crack formation,[187] and delamination[103] (Fig. 12). Crack pinning is possible only if the crack tip size is smaller than the filler size. Hence, it is rarely observed in the case of nano-fillers but has been reported by some authors.[138,143] The high aspect ratio of graphene sheets coupled with strong filler-matrix interaction causes the crack to change its path leading to crack deflection. The crack continues to propagate after undergoing deflection, but now the crack propagation occurs at different heights. This leads to off-plane loading conditions, generating a coarse, multiplane fracture surface area, thereby contributing to enhanced fracture properties.[103,107] When crack deflection occurs, the crack tends to tilt and twist and crack growth occurs in mixed mode. As a result, more fracture energy is spent than only mode I manifesting as a higher fracture toughness in the graphene-based epoxy composite.[106,188]

As was highlighted above in Section 2.3, the filler dispersion, interaction of the filler with the matrix and the nature of the interface between the two play a crucial role in enhancing the

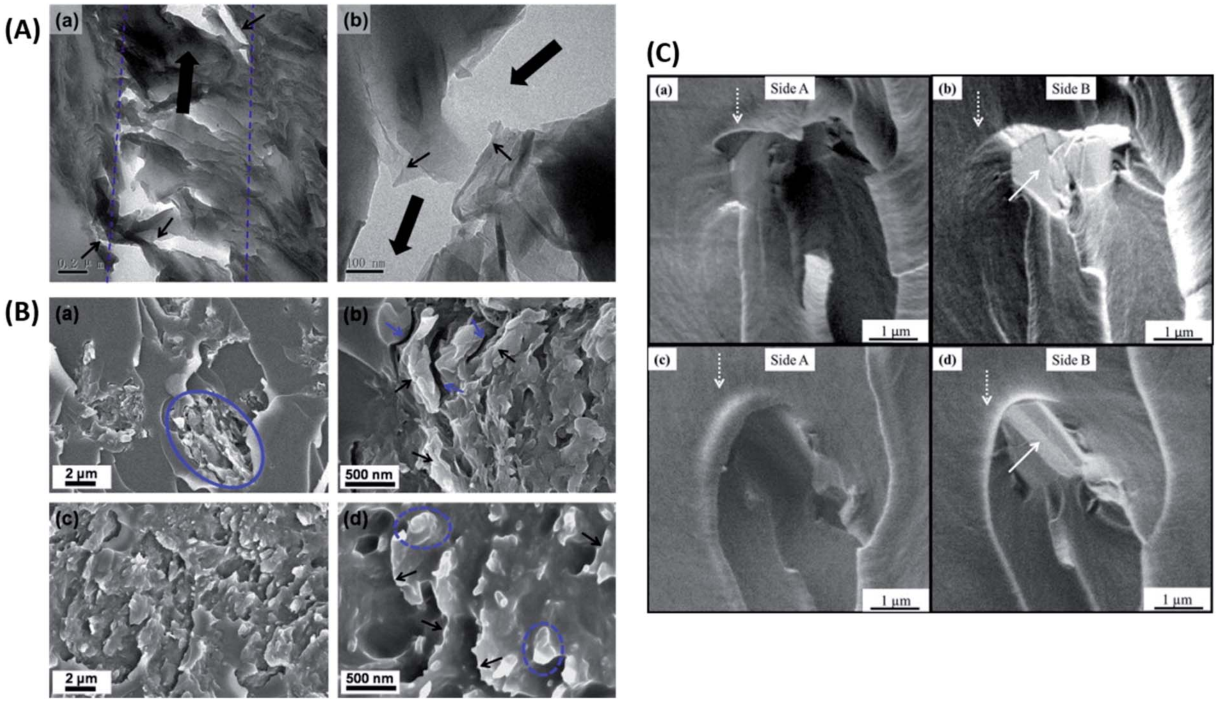

Fig. 12 (A) TEM images of nanocomposites displaying crack bridging (a and b), crack deflection (b) and delamination (b) of GO.[66] Reprinted with permission from ref. 66 (Copyright © 2014 Elsevier Ltd). (B) SEM images of fractured epoxy composite samples showing poor adhesion in the case of graphene/epoxy (a and b) and strong adhesion in Triton–graphene/epoxy (c and d).[60] Reprinted with permission from ref. 60 (Copyright © 2013 Elsevier Ltd). (C) Toughening mechanisms in epoxy composites containing GNPs (a and b) and TRGO (c and d), the white arrow indicates the delaminated surface of the nano-filler.[103] Reprinted with permission from ref. 103 (Copyright © 2014 Elsevier Ltd).

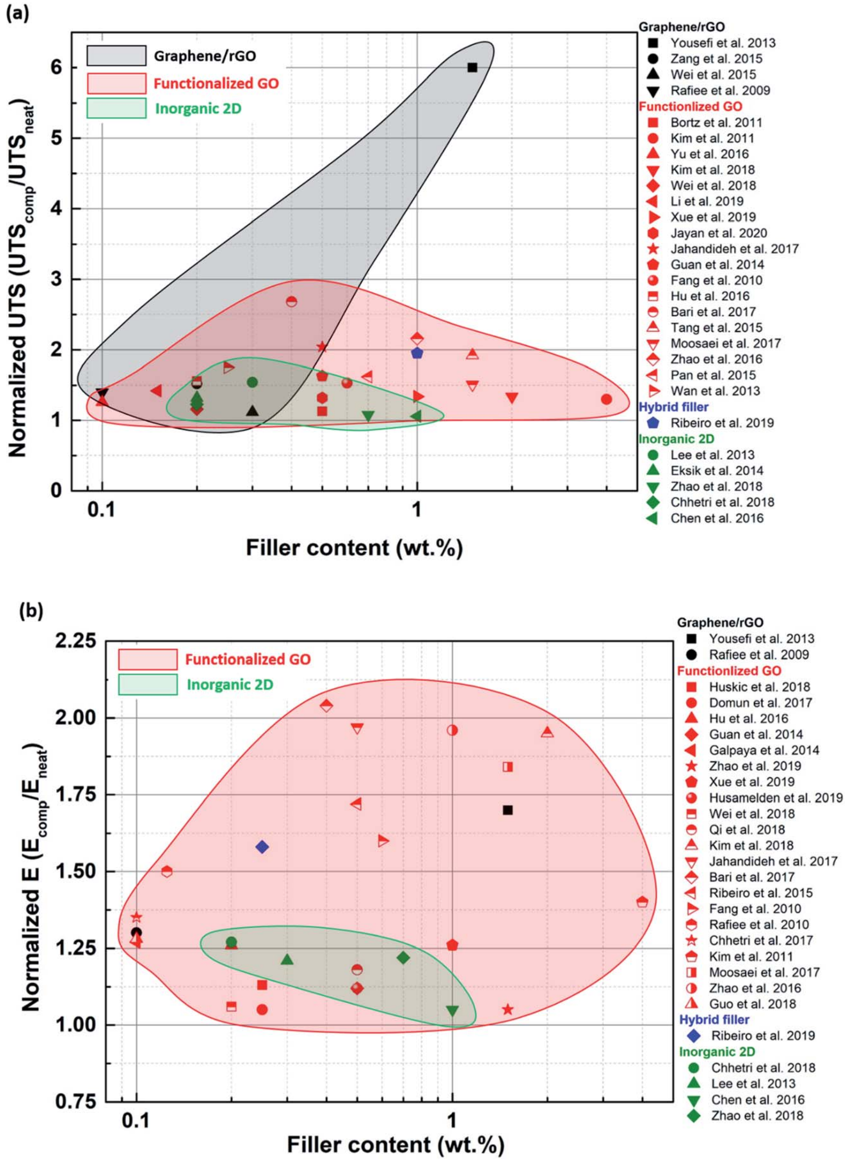

Fig. 13 Normalized UTS (a) and *E* (b) plotted against filler loading for various types of fillers to compare the effects of each type of filler.

fracture properties of the composite.[70,116] To improve the filler matrix interaction, functionalization of the filler is the most preferred route.[189] Wan *et al.*[60] have shown that the functionalization of graphene improved filler-matrix interaction, hence the fracture properties (Fig. 12B).

The graphene sheets are usually bound to each other due to van der Waals attraction. In the case of strong filler-matrix interaction, the filler is tightly bound to the matrix and does not tear apart from the matrix. In such a case, the graphene sheets can undergo delamination, *i.e.*, the graphitic layers can separate when subjected to a mechanical load (Fig. 12C). This separation of graphitic layers allows the crack to eventually penetrate the layers to give rise to a dimpled fracture surface. All these factors contribute towards increased fracture surface area and hence towards improved fracture properties.[103] Stress whitened zones are a way to assess the extent of toughening because they indicate the filler matrix interaction. The larger the stress whitened zone, the more the energy dissipated and the better the fracture properties.[185,190]

5. Comparison of epoxy composites containing different 2D nanofillers based on mechanical and thermal properties

A wide range of 2D materials, including graphene, inorganic 2D nano-sheets and their various hybrids, are being widely studied for reinforcing epoxy composites. It is evident from the literature survey that functionalized graphene has outperformed the other types of fillers in terms of enhancements observed in tensile, fracture and thermomechanical properties. Graphene oxide can be easily functionalized due to carboxyl and hydroxyl groups attached to its surface. The ease of synthesizing such

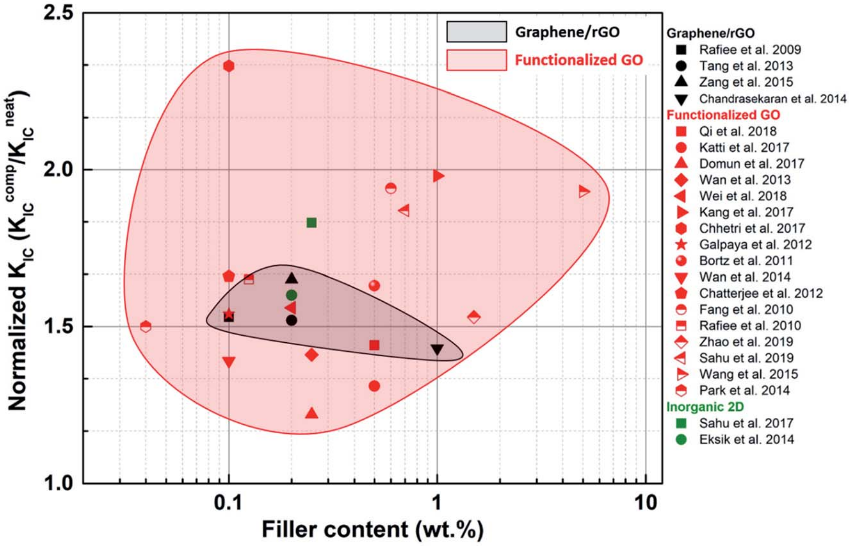

Fig. 14 Comparison of the effect of various 2D fillers on the fracture toughness K_{IC} of epoxy composites.

fillers and their compatibility with various organic solvents have rendered functionalized GO a preferred option for reinforcing epoxy. However, TMDs have also shown promising improvements in the mechanical properties of epoxy composites. TMDs are the go-to option, especially when mechanically strong and electrically insulating polymer composites are required. Hybrid fillers have started to gain popularity in the last few years, especially multiscale hybrids. Hybrid fillers can prevent restacking and agglomeration of 2D nano-sheets by introducing and retaining gaps between the sheets.

Functionalized graphene performs better than blank graphene because it can be uniformly dispersed in the matrix due to the favorable interactions between the functionalizing species and the matrix. As a result, a stronger filler-matrix interaction is established while preventing agglomeration. Sometimes, the functionalized filler can contain primary and secondary amine groups, which act as secondary hardening agents and trigger epoxy curing reactions. As a result, the interface between such a filler and the matrix is further strengthened. When polymer grafted GO is used as a filler, the polymer chains attached to the sheet inhibit agglomeration and ensure uniform dispersion of the sheets in the matrix. However, an exception was observed where an unmodified filler also showed improvements in mechanical properties (Fig. 13). Yousefi *et al.*[149] used reduced GO to produce a remarkable improvement in tensile properties. Since the reduction was carried out *in situ* using hydrazine, it was concluded that the oxygen functional groups left behind on the surface of rGO after reduction were responsible for bringing about effective load transfer.

As compared to the other 2D materials, graphene has the highest inherent modulus, breaking strength and fracture toughness. Although functionalization of graphene improves dispersion, it can introduce defects and lower the inherent mechanical properties. Despite this, it is still evident that graphene performs better than inorganic 2D materials when it comes to enhancement in tensile properties. Functionalized graphene was capable of improving tensile properties in a broader loading range. Non-functionalized inorganic 2D nanosheets are more susceptible to agglomeration, and hence their loading needs to be restricted below the agglomeration threshold. Inorganic 2D nano-sheets are very often much smaller in lateral size than graphene sheets. As a result, the aspect ratios of graphene and its derivatives are higher than the inorganic 2D nano-sheets. Hence, better load transfer can be achieved in the case of graphene (Fig. 13).

Fracture property improvement ranging from 20% to >100% can be achieved using fGO as a filler, even at low loadings (Fig. 14). Improvements reported for blank graphene or rGO were much less than those reported for fGO, implying that better dispersion and load transfer occurs when the filler surface is modified. In exceptional cases such as Wu *et al.*,[100] nearly 900% improvement in G_{IC} was achieved for non-functionalized GNPs. The electrically conducting nature of graphene flakes was utilized to align them in a particular direction. As a result, the maximum toughening effect was observed when the direction of crack propagation was perpendicular to the graphene wall.

Irrespective of the combination of hybrid filler used, it has consistently been reported that the agglomeration and stacking of 2D nano-sheets can be successfully prevented by introducing another filler that acts synergistically with the 2D nano-sheet. The hybrid filler is capable of better filler matrix interaction due to reduced restacking and agglomeration issues. As a result, low loadings of hybrid fillers are also capable of significantly enhancing the fracture properties.

Mechanical properties like tensile and fracture strength are often studied at room temperature. To get some insight into the behavior of the epoxy composites at high temperatures, dynamic mechanical studies are a good way of qualitatively establishing the thermomechanical properties of epoxy composites and accurately determining their glass transition temperature.

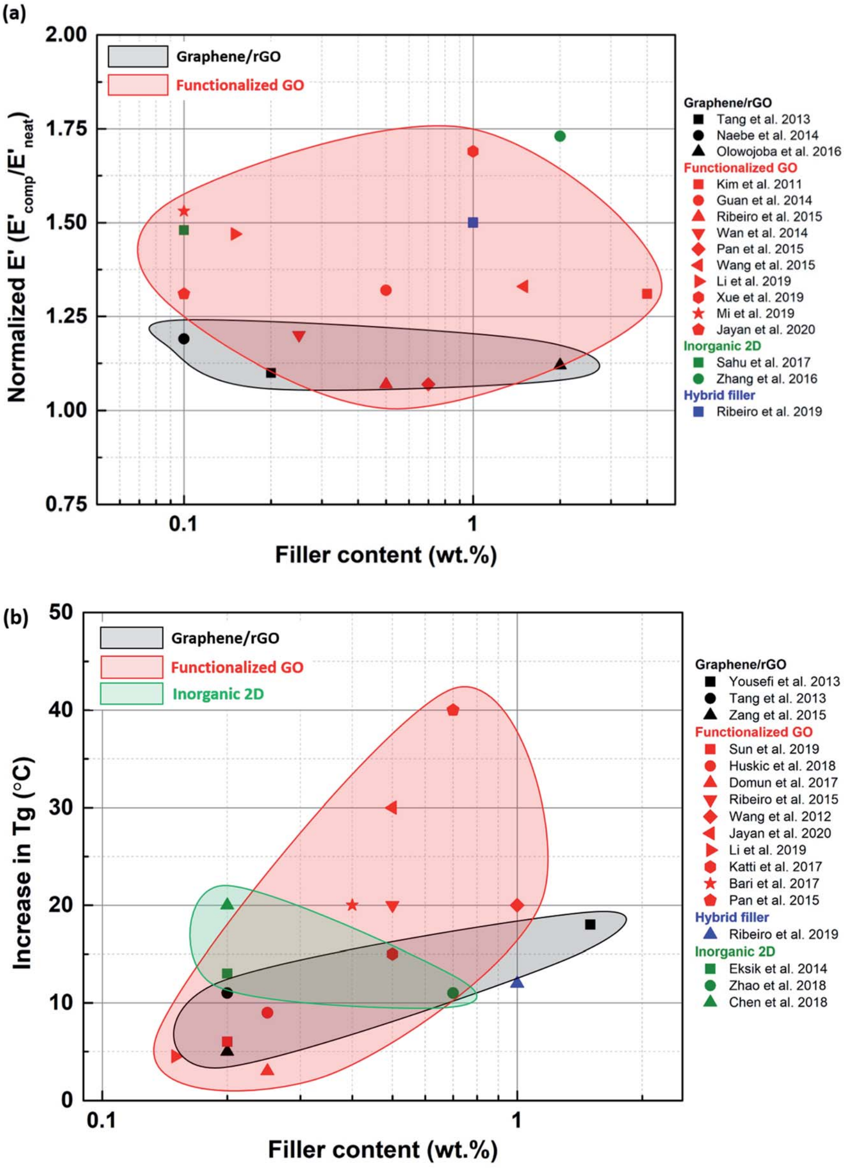

Fig. 15 Effect of filler type and loading on E' at 100 °C (a) and T_g (b) of epoxy composites.

Especially in the aerospace industry, the material undergoes multiple thermal cycles, and hence thermomechanical studies can offer useful conclusions. Dynamic mechanical analysis (DMA) studies have not been extensively conducted for epoxy composites. The data available are scattered, and no consistency was observed (Fig. 15). The available data showed that functionalized fillers perform better, implying that stiffness is dependent on the filler matrix interaction. In the case of inorganic and hybrid fillers, more data are required to draw solid conclusions regarding the thermomechanical behavior. Thermal studies are often neglected or compromised during the synthesis of composites for structural applications. But, it is important to focus on improving thermomechanical properties simultaneously with the other mechanical properties.

T_g is often considered to be an indicator of the network density of the composite. The addition of a filler affects the cross-linking of the resin, in turn influencing the T_g. Especially in the case of amine-modified fillers, the filler performs multiple functions. Hence, when amine groups with a chemical structure similar to the hardener are attached to the filler, they tend to modulate the stoichiometric ratio around the filler to form a hierarchical structure. This structure can then influence the mobility of the epoxy chains around the filler, thereby affecting the T_g.

6. Challenges

6.1 Lack of unanimity related to the influence of filler size on composite properties

In nanoparticle reinforced composites, the filler's aspect ratio is a crucial parameter that affects the filler-matrix interaction and drives the matrix toughening mechanisms. The effect of filler size on the mechanical properties of epoxy composites was studied in depth by some research groups.[191] Kim *et al.*[189] studied the effect of non-oxidized graphite flakes (f-NOGFs) functionalized using potassium sodium tartrate tetrahydrate on epoxy resin. f-NOGFs were sorted into three different sizes ($L = 0.25$, 0.75 and 1 μm, $t = 4$ nm). It was reported that the epoxy composites containing f-NOGFs of size 1 μm showed the best tensile properties among the three. The E, UTS, and tensile toughness improved by 31%, 99%, and 230% than the neat epoxy at 0.6 wt% loading. This behavior was attributed to the large interfacial area of interaction between the matrix and the filler. Since the oxidation route was not followed for surface modification, the graphene flakes were relatively defect-free compared to GO, and their inherent strength was preserved. Similar results were reported by other authors.[68,190] Huskić *et al.* reported that GO synthesized from expanded graphite of size 1200 μm displayed better tensile strength and T_g than GO from expanded graphite of size 130 μm. Alexopoulos *et al.*[190] reported that among the two GNP types (grade C $t = 2$ nm $L = 2$ μm and grade M $t = 6$ nm and $L = 15$ μm), the larger GNP sheets showed an 18% higher UTS at 0.25 wt% as compared to 11% improvement for the composite containing smaller GNPs. Larger GO sheets connected better with the epoxy matrix and brought about efficient load transfer. In another study,[192] the size effect of commercially available graphene nanoplatelets (GNPs) of two different sizes ($L = 5$ μm and 25 μm) on the fracture properties of epoxy was evaluated. An improvement of 82% and 60% in the fracture toughness was observed for large and small GNPs at a loading of 2 wt%, respectively. It was concluded that large-sized graphene sheets are capable of deflecting and bridging the advancing crack. However, the reverse was reported in ref. 185. It was observed that out of three different sizes ($L = 10.79$, 1.72, 0.7 μm, $t = 15$–30 nm), the smallest GO flakes gave the best fracture toughness, 75% higher than the neat resin, at 0.1 wt% loading. The larger sheets tend to have more wrinkles and folds and are likely to affect the filler's load-transfer ability and act as stress concentrators during fracture.[193] Fractography analysis showed that the smallest-sized GO showed the maximum resistance to crack propagation compared to the other two sizes. It was therefore concluded that the fracture properties are inversely proportional to the size of the flakes. These results were in sync with the simulation results reported by Zhao *et al.*[194] They reported an increase in stress concentration in the matrix with a decrease in the filler size at a constant loading. Shokrieh *et al.*[195] compared the reinforcing effects of graphene nano-platelets (GPLs $t = 3.5$ nm and $L = 40$–120 nm) and graphene nanosheets (GNS $t = 6$–8 nm and $L = 5$–8 μm) to understand the effect of filler geometry on the fracture toughness of the composite. The fracture toughness improved by 39% and 16% for 0.5 wt% GPL/epoxy and GNS/epoxy composites, respectively compared to the neat resin. Tensile modulus improved by 10% for 0.5 wt% GPL/epoxy composite. GPLs performed better than GNS due to higher surface area of interaction with the matrix and lower thickness.

Graphene nano-sheets falling in a wide size range (40 nm to 25 μm) have been used by various research groups. The terms ‘large’ and ‘small’ have been used for a very wide size range on a relative scale. There are no well-defined size brackets to classify graphene sheets as ‘small,’ ‘medium’ or ‘large’ sheets. As a result, it is difficult to draw clear conclusions related to the effect of the size of 2D fillers on the mechanical properties of epoxy composites. There is a need for standardization of nanomaterials based on the size and thickness and other crucial properties such as purity, surface roughness *etc.*,[196] which is discussed in detail in Section 6.5 below.

Moreover, many factors such as the resin's type and properties, the functionalization level of the filler, loading conditions, composite fabrication method, curing schedule, *etc.* affect the final properties of the epoxy composite. Hence, no solid conclusion can be drawn from the literature mentioned above about the size effect of the filler on epoxy composites because it is subject to a number of other factors.

6.2 Filler dispersion: methods, characterization and challenges

Solution mixing is a very widely used dispersion technique due to the filler's affinity to organic solvents.[143,197] However, solution mixing involves using organic solvents, which can cause degradation of the composite properties if not completely removed before curing. Atif *et al.*[187] studied the effect of retained acetone in multilayer graphene (MLG) reinforced epoxy composites. Epoxy composites were synthesized using three dispersing media: MLG in the hardener (MH), MLG in epoxy (ME) and MLG in acetone (MA). The best mechanical properties were observed for the MH-type composites. At 0.3 wt% of MH, the impact toughness, young's modulus and flexural modulus increased by 89%, 24% and 46%, respectively, compared to neat epoxy. The K_{IC} and G_{IC} improved by 29% and 7%, respectively, at 0.1 wt% MH loading. It was reported that trace solvent (acetone) could weaken the epoxy chains, give rise to porosity and act as stress concentration sites, degrading the T_g and mechanical properties. On similar lines Chong *et al.*[191] studied the effects of residual solvents on the properties of epoxy composites. The authors reported that the residual solvent THF and NMP in epoxy composites lower the T_g significantly (>50 degrees), the effects being more profound for NMP. The residual solvent also lowered the tensile properties. However, the fracture toughness and fracture energy both increased for composites containing residual solvents. This might result from lower cross-linking because the solvent inhibited the curing reaction of epoxy to some extent. The lower cross-linking results in lower brittleness and thereby improved fracture properties.

It is noteworthy that the industries do not approve of the solvent-based approach because solvent removal adds an extra step, consuming extra time and increasing the cost. Also, improper disposal of solvents can cause damage to human health and the environment. Hence solvent-free methods for composite fabrication like direct addition of the filler to the hardener or resin using high-speed shear mixing or ultrasonication,[71,147] three roll milling,[198,199] phase transfer methods,[110] resin impregnation[176,178] *etc.* are being studied. Three roll milling performs a dual function when a resin–filler mixture is subjected to shear forces acting between three

Table 6 Commercial graphene composite products

Product	Model name	Sector	Company	Application	Year	Attributes	Nano-material used
Tennis racket	Youtek Graphene Speed S Series	Sports	Head	Structural	2013	Improved strength to weight ratio	Graphene
Skis	Joy	Sports	Head	Structural	2014	Improved strength to weight ratio	Graphene
Tennis racket	Graphene XT	Sports	Head	Structural	2015	Improved strength to weight ratio	Graphene
Bicycle wheel	Quarno	Sports	Vittoria	Thermal	2015	Improved heat dissipation	Graphene
Bicycle	Interceptor graphene	Sports	Dassi Bikes	Structural	2016	Improved strength to weight ratio	Graphene
Sports shoes	G-series shoes	Sports	Inov-8 & Manchester University	Structural	2018	Improved strength and flexibility	Graphene
Epoxy paste adhesive	AGM TP300 AGM TP400	Manufacturing	Applied Graphene Materials	Thermal	2019	Thermally conductive polymer material	Graphene
3D printing filament	Koltron G1	Manufacturing	Graphmatech & Add North	Thermal	2019	Thermally conductive polymer material	Graphene
Nylon Aros graphene pellets	Aros Create	Manufacturing	Graphmatech	Structural	2019	Electrical and tribological properties	Graphene
Bullet proof vest	2AM line	Defence	Planar Tech	Structural	2020	Improved strength to weight ratio	Graphene + UHMWPE
Bicycle wheel	Eagle F1	Sports	Goodyear	Structural	2020	Improved strength to weight ratio	Graphene + amorphous spherical silica

cylindrical rolls. It exfoliates multiple-layer sheets into few layers *in situ* and ensures uniform dispersion in the epoxy matrix without additives or solvents.

Nonetheless, if the shear forces in the solvent-free dispersion methods exceed the optimum limit, it can introduce defects in the graphene sheets and weaken the composite. Industries

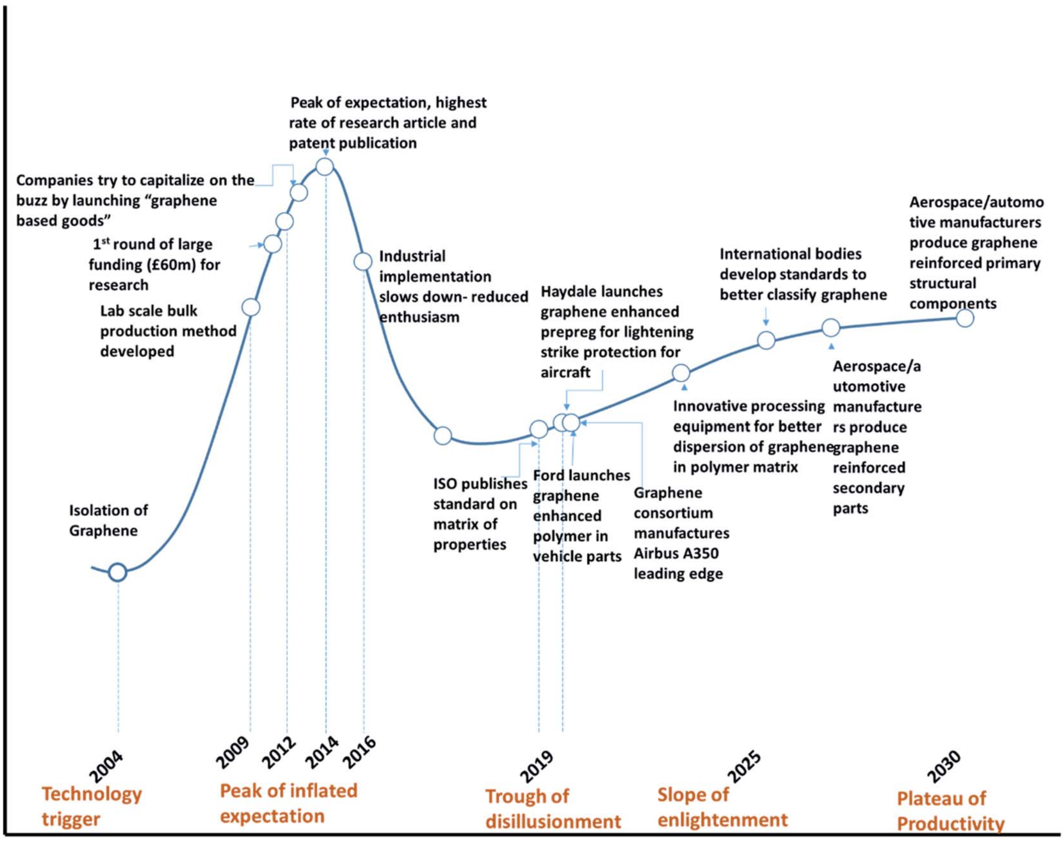

Fig. 16 Gartner hype cycle for graphene based polymer composite product commercialization.[205,206]

encourage solvent-free methods for dispersion because it reduces industrial waste and the risk of hazards. However, solvent-free methods are difficult to scale up while maintaining the quality of dispersion. Hence, new techniques which can achieve homogeneous dispersion without the risk of hazards need to be explored.

A wide range of characterization methods have been used to confirm the state of dispersion of the graphene filler in the epoxy matrix. Optical,[70] electron[68,104] and atomic force microscopy[71] techniques are commonly used to visually comprehend the dispersion state of the filler. However, at low loadings ($\leq$0.1 wt%), it can be difficult to study dispersion using microscopy techniques since a layer of epoxy resin might shield the filler.[106] As a result, other methods were considered. It was reported by Hu *et al.*[145] that a high-intensity D band in the Raman spectra was an indication of graphene agglomeration. Similar results were reported in ref. 200 and 201. Eksik *et al.*[151] reported a novel confocal Raman imaging method for evaluating the dispersion state of MoS_2 nanoplatelets in epoxy resin. Since uniform dispersion of pristine TMDs is challenging at high loading levels, significant agglomeration was observed beyond 0.3 wt% loading.

XRD is an effective tool to analyze the degree of exfoliation of graphene in the epoxy matrix at low loadings.[70,121,140,202,203] Qi *et al.* used the XRD tool to study GO exfoliation. The XRD curve of unmodified epoxy displayed a broad diffraction peak in the range of $2\theta = 8$–30, corresponding to cured epoxy. The diffraction curve of GO/epoxy and HBPA–GO/epoxy composites also contained the same broad peak of epoxy, but the characteristic peak of GO and HBPA–GO were absent, thereby indicating efficient exfoliation. It is noteworthy that good exfoliation does not indicate good dispersion, and hence other techniques must be used to confirm the dispersion state.[125] Chen *et al.* performed UV-vis spectroscopy on 2 mm thick samples of MoS_2/epoxy composites. It was reported that amine-f-MoS_2/epoxy composites displayed a 10% transmittance against 56% and 65% transmittance of 0.5 wt% MoS_2/epoxy composites and neat epoxy, respectively, thereby indicating that the dispersion state of amine-f-MoS_2 in epoxy was more uniform than pristine MoS_2.[83]

SEM and TEM remain the most popular methods for visually evaluating the filler's dispersion state in the matrix. However, the area under consideration during microscopy analysis is of the scale of microns and is extremely small as compared to the end product. Even if the dispersion appears uniform under the microscope, one cannot be certain that it is uniform throughout the sample. Therefore, it is still challenging to evaluate filler dispersion inside the matrix with total certainty and reproducibility.

6.3 Industry scale-up and commercialization

After the discovery of graphene in 2004, researchers have been making continuous efforts to utilize the full potential of this revolutionary nanomaterial. Graphene has turned out to be the torchbearer for other nanomaterials such as TMDs (*e.g.*, WS_2, MoS_2, $MoSe_2$, and WSe_2), which have also garnered attention. However, after years of effort the most important question remains unanswered. When will the world witness the game-changing 2D nanomaterials being used in real applications?

The use of 2D nanomaterials in advanced composites for industrial applications is still at a very early stage. However, as the understanding of material properties, processing requirements, and raw material availability has improved over the years, some industries have started to adopt these new materials. Despite few industrial implementations that the 2D nanomaterials have found, especially in the sports industry (Table 6), these new promising nanomaterials have not delivered to their hype yet. Moreover, there is no clarity on what type of graphene derivative is used in commercial sports goods. Whether it is monolayered or multilayered, non-functionalized or functionalized or small or large graphene sheets is ambiguous. Also, there have been very few developments where graphene has been used in commercial aerospace or automotive products. Notably, in 2019 Aernnova (Álava, Spain), Grupo Antolin-Ingenieria (Burgos, Spain) and Airbus (Toulouse, France), working as partners for a Graphene Flagship (Gothenburg, Sweden) consortium funded by the European Union, manufactured Airbus A350 using graphene-enhanced resin in the form of CFRP. It was reported that this effort led to the development of lightweight composites resulting in fuel saving. UK-based prepreg manufacturer, Haydale launched a graphene-modified prepreg material for lightning strike protection of aircraft. In the case of the automotive industry, there is one industrial implementation by Ford worth noticing. Ford revealed in 2019 the use of graphene-enhanced foam in their Ford F-150 and Mustang vehicles. It was reported that the use of graphene led to a 20% increase in mechanical properties along with 17% and 30% improvement in noise reduction and heat endurance, respectively. However, the 20% improvement in mechanical properties is far from the 50% to more than 100% improvement in mechanical properties reported in most graphene-based polymer composite studies reported in the literature. The important question that needs to be

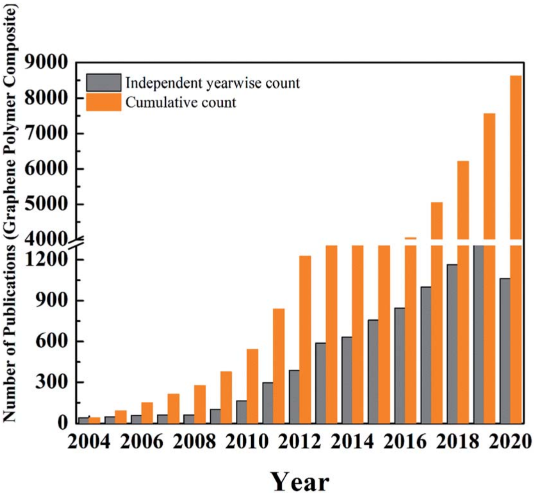

Fig. 17 Statistical graphs showing cumulative and year wise independent number of publications related to graphene (data source: Pubmed).

answered is what is stopping the manufacturers from utilizing these nanomaterials to their full potential and what is the bottleneck for the aerospace and automotive industry-wide adoption of these materials?

6.4 2D materials – the hype cycle

Gartner Inc. introduced the hype cycle model, which explains the journey of a technological innovation going through the peak of hype and reaching realistic scenarios where the technology finds a way for final implementation with respect to time. The hype curve is applicable to 2D nanomaterials including graphene. Fig. 16 shows the Gartner hype cycle for graphene and graphene-based materials.

Since the isolation of graphene by Novoselov of Manchester University in 2004,[204] researchers were curious, and various groups were trying to find the potential for numerous applications. Fig. 17 shows the initial trend in several publications between 2004 and 2009. There was a steady increase in the number of studies and publications. However, when Novoselov received the Nobel Prize in 2010, there was a sudden jump in the number of publications. The number of publications increased fourfold between the years 2009 and 2014. This was the peak of the hype cycle for graphene. This was also the time where many sports goods manufacturers developed "graphene-enhanced" products. Few commercial goods manufacturers claimed to utilize graphene to improve strength. The year 2013 onwards, many sports goods manufacturers launched products such as tennis rackets, golf clubs, bicycle structures, *etc.*, that claimed to have used graphene for improved strength and improved weight to strength ratio. However, the exact details of the graphene nanomaterials used in these products were not clear.

Table 6 shows the list of commercial products, which have graphene components incorporated for structural applications. This is indicated by the phase between year 2012 and 2013 in the "hype cycle" where few companies tried to utilize the buzz around the new technology. Between 2016 and 2018, there was a steady increase in the number of patents and publications related to graphene-based materials (Fig. 17) and continued funding for academic and industrial research. However, there were no major announcements by the big players in aerospace and automotive companies to utilize graphene to improve the performance of the structural component of the products. This was typical of the trough region of the Gartner hype curve shown around the year 2016 (Fig. 16). The current scenario places graphene-based polymer composite research in the "slope of enlightenment region" shown in the timeline between 2019 and 2021 in Fig. 16, where industries find practical application with realistic goals to enhance the properties by using graphene and other 2D material reinforced composites. Though the number of such instances is still extremely small, a more systematic approach will increase confidence building for structural application in various industries.

6.5 Lack of standardization of graphene and other 2D materials

One of the most important reasons behind the lack of confidence in implementing graphene in industrial applications is the uncertainty regarding the reproducibility of the results. The final graphene reinforced composite properties vary

Table 7 Worldwide commercial manufacturers of graphene/CNTs/2D nanomaterials

Sr. no.	Manufacturer	Nanomaterial product	Country of origin
1	Nanocyl	CNTs	Belgium
2	6 Carbon Technology	CVD grown TMDs 2D films, graphene, hBN	China
3	Shenzhen Nanotech	CNTs	China
4	2D Carbon Tech	Graphene	China
5	Arkema	CNTs	France
6	Ad-nanotech 2013	Graphene, MWCNTs	India
7	Hexorp	Graphene, graphene oxide, reduced graphene oxide	India
8	Abalonyx	Graphene oxide, graphene oxide derivatives	Norway
9	Advanced Graphene Products	Graphene, graphene oxide, reduced graphene oxide	Poland
10	Akkolab	Graphene oxide and reduced-GO materials	Russia
11	2DM	Graphene flakes	Singapore
12	Graphenea	Graphene oxide	Spain
13	2D Fab AB	Graphene flakes	Sweden
14	Applied Graphene Materials	Graphene	United Kingdom
15	Cambridge Nanosystems	Graphene	United Kingdom
16	Directa plus	Graphene	United Kingdom
17	Haydale	Graphene	United Kingdom
18	Nanointegris	Graphene, CNTs, boron nanotubes	USA
19	Nano C	CNTs	USA
20	G6 Materials Corp.	Graphene	USA
21	2D Semiconductors	CVD grown TMDs	USA
22	XG Sciences	Graphene	USA

significantly with average sheet size, distribution level and extent of functionalization of graphene, *etc.* From the literature on graphene-reinforced polymer composites, it is clear that reproducing the batch with mechanical and thermal properties is extremely difficult because of dependency on the aforementioned parameters. This is one reason behind the disparity in the extent of improvements in mechanical properties reported by different research groups. The aerospace industry works on very stringent regulations and guidelines imposed by the respective aerospace regulatory bodies of every country, as the safety of passengers is at stake and depends on the reliable performance of aircraft parts during service. Hence, the aerospace industry requires a robust material system, which should be reproducible. In a recent article, Terrance Barkan, executive director of Graphene council explained in depth the challenges about the issue of absence of "standard grade" of graphene and any reference materials.[206] He also emphasized the lack of transparency regarding the grade of graphene being used by manufacturers. Many companies are manufacturing and supplying graphene and other 2D nanomaterials on a commercial scale (Table 7). Some of the companies also provide the relevant material characterization details such as XRD and SEM data. However, the user still has to perform additional characterization to understand the complete properties of the 2D nanomaterials. It may be relatively easier for researchers to validate the data provided by these companies, as most research institutes have the required characterization equipment such as XPS, XRD, FTIR, SEM and TEM *etc.* However, it may not be possible for industries to do such a verification because of the inaccessibility of the required resources. Also, some 2D nanomaterial manufacturers do not provide any insight about the type of graphene platelets in terms of the average number of layers, sheet size, functionalization and on the other hand, some other manufacturers provide "their own" classification and different companies give different names for the different 2D nanomaterial variants. Hence it is extremely important for international testing standards development bodies to pay attention to this need and develop dedicated standards for these unique materials similar to other conventional materials.

In 2019, ISO released a standard[207] specifically for graphene and 2D materials titled "ISO/TR 19733:2019 Nanotechnologies—Matrix of properties and measurement techniques for graphene and related two-dimensional (2D) materials" which related properties of the graphene & other 2D materials to measurement techniques using a matrix. In future, more such initiatives to standardize and classify the 2D nanomaterials will pave the way for true commercialization of graphene for all the applications envisioned by the researchers. And industries like aerospace will be more likely to adopt these "wonder materials" for potential weight saving (Fig. 18).

6.6 Health hazards

As we move towards further commercialization of graphene and other 2D material-based products, a very important question needs to be answered. Are 2D materials safe for humans and the environment? Since the discovery of CNTs and graphene, few studies have focused on the interaction of these materials with biological systems and their cytotoxicity. The researchers have brought attention to the risk of occupational exposure to 2D materials. The most probable scenario of occupational exposure of humans to 2D materials is during the industrial production or disposal of lab/industrial waste *via* inhalation, ocular, cutaneous or oral routes (Fig. 19A). The inhalation route is the most studied route among the others.

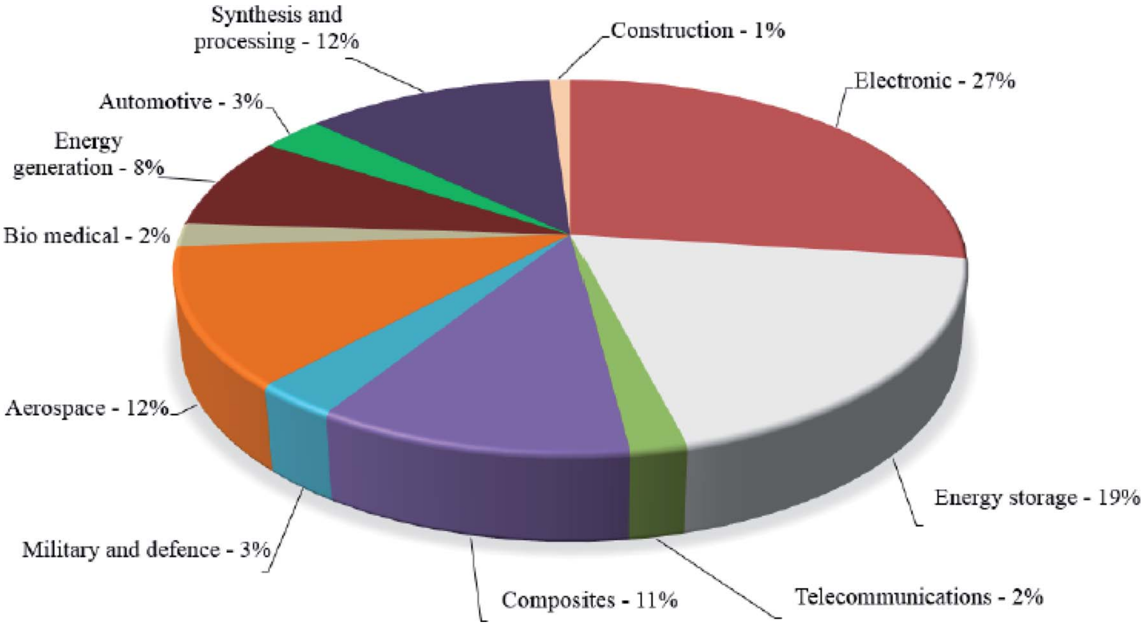

Fig. 18 Commercial applications of graphene-based materials.[208] Reprinted with permission from ref. 208 (Crown Copyright © 2017 Published by Elsevier Ltd).

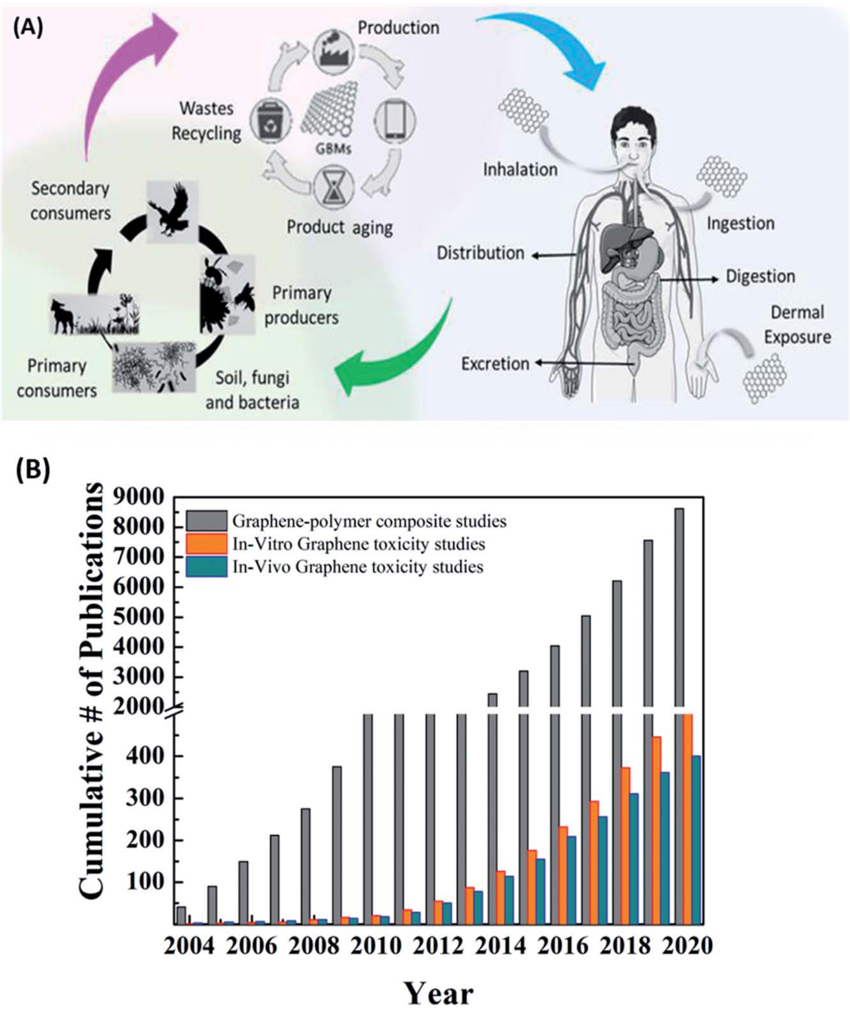

Fig. 19 (A) Schematic showing health and environmental hazards of graphene exposure.[223] Reprinted with permission from ref. 223 (Copyright © 2018, American Chemical Society). (B) Comparative chart of the number of publications for graphene/graphene derivative-polymer composites with the number of publications on *in vivo* and *in vitro* toxicity studies.

The ability of graphene and other 2D materials to exist in a form as thin as an atom and yet remain mechanically strong and robust is as problematic as it is exciting. This very nature of these 2D "nano" materials imparts the property of being airborne and poses a big risk of getting inhaled while working with these materials. Once settled in the lungs, these materials may lead to cytotoxicity and initiate cell damage. One of the initial studies about the cytotoxicity of graphene and graphene oxide was conducted by Zhang *et al.*[209] The authors performed the studies *in vitro* and provided exposure to cell lines with graphene and CNT concentration ranging from 0.01 μg ml^{-1} to 100 μg ml^{-1} for 24 h. The study showed accumulation of graphene platelets on cell membranes after 24 h of exposure, and exposure to CNTs shows a relatively greater cellular membrane damage. *In vitro* studies have demonstrated that functionalization of graphene with biocompatible functional groups and polymers decreased the cytotoxicity of these materials.[210] The review about the cytotoxicity of graphene and graphene oxide by Seabra *et al.*[211] revealed that many factors such as concentration, functionalization, number of layers, time of exposure and synthesis route affect the toxicity of graphene. There is consensus about the mechanism of toxicity in biological systems by carbon and other nanomaterials. One of the mechanisms is *via* oxidative stress in cells. Oxidative stress occurs in cells when there are excess of free radicals, which may damage cells, proteins, DNA, *etc.* Oxidative stress occurs *via* the formation of reactive oxygen species (ROS). Another mechanism is the possible cell membrane damage by the sharp edges of the sheets of 2D materials.[212] Many *in vitro* studies have shown toxic effects of graphene and GO in lung cells, skin cells and stem cells.[213–218] Several *in vitro* studies show no toxic effect of graphene and GO on cells.[219–221] Hence there are conflicting conclusions from *in vivo* studies about the cytotoxicity/biocompatibility of nanomaterials, especially CNTs and graphene materials. Xiaoli *et al.*[222] have published a comprehensive review that provides detailed insights from the literature to date from *in vitro* and *in vivo* studies. The authors have conveyed that despite many research groups working to study the toxicity of the nanomaterials (Fig. 19B), it is difficult to arrive at any conclusion because of the lack of dependable experimental models and evaluation standards.

Additionally, due to the lack of standardization of graphene grades and other 2D materials, it is difficult to understand to which 2D nanomaterial is the toxicity study applicable, since graphene produced by one research group could differ from the one produced by another research group. The variations could arise from a difference in the number of graphene layers, length and width of graphene sheets, and the difference in the C to O ratio. Hence, it's very difficult to compare the results obtained by different research groups, leading to conflicting observations. Therefore, there is an urgent need for more research to evaluate the toxicity of graphene and other nanomaterials for human exposure.

7. Conclusion

Several 2D nano-sheets, including graphene and its derivatives, TMDs, hBN, MXenes, *etc.*, have been studied as reinforcements for epoxy composites to enhance their mechanical performance. Among these nano-sheets, graphene derivatives have been on the lead due to many reasons: (i) ease of synthesis through the chemical route, (ii) ease of functionalization, (iii) inherently higher modulus and strength of graphene as compared to other 2D materials, (iv) compatibility with organic solvents and (v) higher aspect ratio. The literature available on epoxy reinforced with inorganic 2D nano-sheets is scarce in comparison to graphene reinforced epoxy. However, some authors have proven that TMDs and hBN can produce remarkable improvements in the mechanical properties of epoxy composites. TMDs are especially useful because of their high bandgap, when an electrically insulating and mechanically robust polymer composite is required. Recently, the use of hybrid fillers has become popular because the merits of two different fillers can be synergistically combined to achieve toughened epoxy composites. Not just that, the nature of multiscale hybrid fillers is such that they form favourable architecture that is capable of establishing a strong filler matrix interaction and hence facilitate better load transfer.

Through this review, we have tried to bring the research community's attention to the challenges and future strategic approach in 2D nano-material reinforced epoxy composites. More focus and work are required in terms of the health and environmental effects of these nanomaterials. Also, the regulatory bodies should come up with standard protocols for disposal of these nanomaterials to prevent any environmental damage.

A clear understanding of the classification based on chemical composition, physical properties, constituents, *etc.*, is available for commercial metal alloys and plastic. There should be efforts to standardize 2D nano-materials like all other standard commercial materials. Since the nature of 2D nano-sheets is different than bulk materials, the classification categories could be based on sheet size and thickness, defects, extent and type of functionalization, purity, *etc.* The standardization will help accelerate the journey of 2D reinforced epoxy composites towards commercialization and industrialization.

As the endeavors to address the challenges mentioned above are pursued, and progress is made, it should also be noticed that industrialization depends on various technologies available for the processing of these nano-materials. As we know, currently, there is no focused effort to develop new technology dedicated to processing these nanomaterials to utilize the full potential of these few atom-thick nano-sheets. Hence, there is a great need to develop solutions and technologies to enable better dispersion of 2D sheets in the matrix for achieving large-scale production while maintaining enhanced mechanical properties.

If the above challenges are addressed in the coming decade, then a revolution can be expected in terms of a larger spectrum of industries successfully utilizing these 2D wonder materials to enhance the performance of their products. We may witness another breakthrough like the one experienced in carbon fiber reinforced epoxy composites implemented for aerospace structural components after 30 years of rigorous research and development by academic and industrial organizations. In the coming decades, if the gap between lab-scale research and industry is bridged, 2D nanosheets can lead the way for extremely light and tough composites to reduce the carbon footprint by enabling aerospace industries to manufacture lightweight aircraft. The automotive and sports industry can also benefit from graphene and other 2D materials if these challenges are systematically addressed.

Conflicts of interest

There are no conflicts to declare.

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