Abstract: Graphene has been ranked among one of the most remarkable nanostructure of the carbon world. Graphene modification and nanocomposite formation have been used to expand the practical potential of graphene nanostructure. The overview is an effort to highlight the indispensable synthesis strategies towards the formation of graphene nanocomposites. Consequently, graphene has been combined with useful matrices (thermoplastic, conducting, or others) to attain the desired end material. Common fabrication approaches like in-situ method, solution processing, and melt extrusion have been widely involved to form the graphene nanocomposites. Moreover, advanced sophisticated methods such as three or four dimensional printing, electrospinning, and others have been used to synthesize the graphene nanocomposites. Focus of all synthesis strategies has remained with the standardized graphene dispersion, physical properties, and applications. However, continuous future efforts are required to resolve the challenges in synthesis strategies and optimization of the parameters behind each technique. As the graphene nanocomposite design and properties directly depend upon the fabrication techniques used, there is obvious need for the development of advanced methods having better control over process parameters. Here, main challenging factors may involve the precise parameter control of the advanced techniques used for graphene nanocomposite manufacturing. Hence, there is not only need of current and future research to resolve the field challenges related to material fabrication but also reporting compiled review articles can be useful for interested field researchers towards challenge solving and future developments in graphene manufacturing.

Keywords: graphene; nanocomposite; synthesis; technique; in situ; melt extrusion

1. Introduction

Due to technical utilizations of graphene nanostructures, considerable literature has been reported on the structure and synthesis methods [1]. Particularly, matrix-nanofiller compatibility has been found important to enhance the optical, electronic, thermal, mechanical, and other important properties of the graphene nanocomposites [2,3]. Consequently, the miscibility effects in the nanocomposite nanostructure resulted in synergistic property improvements in the high-tech nanomaterial [4]. The interfacial interactions in the matrix-nanofiller system greatly depend on the synthesis strategies used [5]. In this context, choice of an appropriate synthesis method may lead to advanced nanocomposite with superior physical features [6]. Traditional methods used to form the polymer/graphene nanocomposites include the in situ, solution, and melt methods [7]. In addition, various efficient advanced processes have been used to form the graphene nanocomposites like printing, spinning lithography, and several
others [8,9]. Consequently, thermoplasts, thermosets, and conjugated matrices have been filled with graphene nanoparticles to attain superior properties and applications [10–12]. The resulting graphene nanocomposites have enhanced physical properties due to suitable processing techniques applied to gain improved interfacial aspects of these nanomaterials [13].

Hence, noteworthy chemical and physical properties, graphene has been widely inspected by the researchers over past decades. Graphene has been used in numerous potential fields due to high surface area, excellent electrical, mechanical, thermal, and other structural and physical characteristics. Consequently, graphene has been found applicable for the energy devices, electronics, sensors, nanocomposites, and biomedical devices, drug delivery, and tissue engineering. To enhance the practical use of graphene nanocomposite in technical fields, it has been found important to fabricate the graphene based materials by opting appropriate synthesis strategies. Advanced fabrication techniques have well controlled parameters to attain specific properties of graphene nanocomposites for desired end application.

This review focuses on the designs and synthesis strategies for the high performance graphene nanocomposites. According to analysis, this article is novel to present manufacturing approaches of novel graphene derived nanocomposites. For graphene nanocomposites, various traditional and modified methods have been used. Developments in the synthesis techniques of graphene nanocomposites can enhanced the technical potential of these nanomaterials. Consequently, the designing, features, and appropriate processes for the graphene nanocomposites have been explained here. Literature research reports so far have been observed on the fabrication of graphene based nanomaterials using appropriate synthesis strategies. However, no compiled review article is seen on technical fabrication techniques and comprehensive debates towards structural developments using modified methods and controlled parameters. Aim or objective of this review is to develop a comprehensive article on the most frequently used methods for graphene nanomaterial synthesis. Accordingly, the resulting graphene nanocomposites have been discussed under numerous categories of solution, melt, and other fabrication techniques, in this article. Then, the design, characteristics, and applications of the nanocomposites have been explained with respect to the fabrication methods used. Thus, such specific overview on graphene nanocomposite fabrication has not seen in literature before with well explained recent literature and outline. Despite the advancements so far, devoted future research efforts are still required on the fabrication of high performance nanocomposite, to overcome the related design and parameter control challenges.

2. Graphene

Graphene is a two dimensional single nanosheet of sp² hybridized carbons [14]. Detection of graphene is linked back to 2004 [15]. Graphene has been formed using many technical approaches like exfoliation approaches, laser method, chemical vapor deposition, and chemical synthesis approaches [16]. Graphene has been explored for range of structural and physical features [17]. Graphene has countless enhanced features including very high Young’s modulus of 1 TPa, electron mobilization of 3000–5000 W/mK, and thermal conductivity of around 200,000 cm²V⁻¹s⁻¹ [18].
Essential properties of graphene have been found to depend on the graphene nanostructure [19]. Owing to van der Waals forces, the nanosheet displays wrinkling effects [20]. To augment the structural features of graphene, the nanosheet has been functionalized to introduce oxygen-bearing groups on its surface [21]. Such surface functional graphene nanosheet with hydroxyl, carbonyl, epoxide, carboxylic acid, etc., groups has been often termed as graphene oxide. Graphene and some linked nanostructures are shown in Figure 1. Graphene and derivative nanostructures own fine electronic, mechanical, thermal, and chemical characters [22]. Consequently, applications of graphene have been observed towards the electronics as well as energy devices and countless other technological sectors [23, 24].

![Graphite to graphene and graphene oxide and interconversions.](image)

**Figure 1.** Graphite to graphene and graphene oxide and interconversions.

### 3. In situ technique towards graphene nanocomposites

One of the simple and efficient methods for the formation of graphene nanocomposites is the in situ polymerization or in situ method [25]. This synthesis strategy has been found effective for better graphene dispersion [26]. Fine nanoparticle scattering in turn generated better interactions in matrix-nanofiller phases [27]. Main benefits of in situ synthesis strategy include the environmental friendliness, use of non-toxic solvent, room temperature processing, and one-step processes involved to form the graphene nanocomposites [28]. Subsequently, countless graphene nanocomposite designs have been reported using the in situ synthesis strategy [29]. In situ technique is a facile, low-cost, and environmentally benign method to physically or covalently functionalize graphene nanosheets. In this method, monomers are in situ polymerized in the presence of graphene or graphene oxide to form the nanocomposites. In situ polymerization has been used as a common method for the polymerization of e-caprolactam monomer to form the polyamide 6 backbone [30]. Adding 1–2 vol.% graphene contents along with e-caprolactam monomer during in situ polymerization resulted in reasonable electrical conductivity of ~0.028 Sm−1. In addition, the resulting in situ polymerized polyamide 6/graphene nanocomposites have revealed the superior thermal conductivity of around 0.27 Wm−1K−1 [31, 32]. In situ synthesis strategy has
also led to enhanced mechanical properties of the polyamide 6/graphene nanocomposites [33]. Elevated tensile strength and Young’s modulus were found with 0.1 wt.% graphene nanofiller addition. The improved properties were accredited to the mutual interactions between the matrix and nanofillers leading to compatibility effects. Xu et al. [33] synthesized the polyamide 6 and graphene derived nanocomposites using in situ polymerization method. The caprolactam monomer was in situ polymerized by the ring-opening polymerization reaction [34]. The reaction was carried out in the presence of graphene oxide nanoparticles to follow the in situ process (Figure 2). This method involved the use of 6 aminocaproic acid for an in situ process. This technique caused fine dispersion of monomers as well as graphene nanoparticles in solvent medium, followed by the in situ polymerization to form the polyamide 6/graphene nanocomposite. Figure 3 displays the stress strain curves of unfilled polyamide 6 as well as 0.01 and 0.1 wt.% nano-additive reinforced graphene nanocomposites. The 0.01 and 0.1 wt.% graphene loaded nanocomposite had tensile strength of 84 and 123 MPa, respectively, relative to neat matrix (56 MPa). Hereafter, the mechanical properties of the nanocomposites were found more than 50% higher than the unfilled matrix. Hence, this method has been suggested to minimize the nanoparticle dispersion responsible for improved features of the nanomaterials.

Figure 2. In situ synthesis strategy of graphene nanocomposite by in situ ring opening polymerization of caprolactam occurring in the presence of graphene oxide [33]. Reproduced with permission from ACS.

Figure 3. Stress strain curves of neat polyamide 6 and nano-graphene (NG) nanocomposites with 0.01 and 0.1 wt.% graphene additions [33]. Reproduced with permission from ACS.
Polystyrene, another commodity thermoplastic, has also been polymerized by in situ technique [35,36]. In the presence styrene monomer and graphene dispersion, in situ polymerization method is applied using surfactants [37,38]. Styrene monomer is absorbed on graphene surface and then polymerized leading to fine dispersion of nanoparticles and compatibility with the matrix [39,40]. In this way, in situ produced nanocomposite had fine interactions leading to high electron conduction, heat stabilization, glass transition, and other improved properties [41,42]. Poly(methyl methacrylate) and graphene derived nanocomposites have also been formed using in situ method and polymerizing the methyl methacrylate monomers [43,44]. Physical as well as covalent bindings have been observed between the poly(methyl methacrylate) and graphene nanoparticles [45]. Reports on waterborne polyurethane and graphene based in situ formed nanomaterials have also been found in literature [46,47]. Here again, interfacial interactions between matrix and nanofiller led to enhanced performance, so depicting the efficiency of in situ technique [48].

4. Solution strategies for graphene nanocomposites

Another common synthesis strategy to form graphene nanocomposites is the solution casting or solution synthesis or solvent based processing approaches [49,50]. Solvent method is a facile and low cost for the formation of graphene nanocomposites [51]. In this technique, polymer is dissolved in a suitable solvent and graphene nanosheets are also dispersed in an appropriate solvent [52]. Both the dispersions are mixed and stirred to form a homogeneous nanocomposite mixture (Figure 4). The nanocomposite formation occurs through the solvent evaporation step. Numerous thermoplastic polymers have been successfully formed by solution technique [53,54]. For example, polystyrene and graphene based nanocomposites have been prepared using the solution processing [55]. N-methyl-2-pyrrolidinone was used as a solvent to dissolve polystyrene and disperse graphene nanoparticles. Addition of 10 wt.% nanofiller enhanced the electrical conductivity of polystyrene matrix to $1.5 \times 10^{-7}$ Sm$^{-1}$ [56]. In this concern, the microstructure and matrix-nanofiller interactions in solution formed nanomaterials have been investigated [57].
Figure 5. (a) Electrical conductivity versus filler content for neat polystyrene (PS) and its nanocomposites; (b) Double-logarithmic plot of electrical conductivity versus $\phi - \phi_c$, where $\phi$ is the filler volume fraction and $\phi_c$ is the percolation threshold; and (c) Transmission electron microscopy image of PS:PLA (6:4) composite with ~0.46 vol.% (~1.0 wt.%) graphene additives. The selective localization of graphene in the polystyrene region is evident from the image [58]. PS/CNT = polystyrene/carbon nanotube; PS = polystyrene; PLA = poly (lactic acid); PS/PLA = polystyrene/poly (lactic acid). Reproduced with permission from ACS.
Qi et al. [58] synthesized polystyrene/graphene, polystyrene/graphene/poly(lactic acid), and polystyrene/carbon nanotube nanocomposites using solution strategy. Figure 5 demonstrates increase in the electrical conductivity of the polystyrene/graphene nanocomposites with the addition of 0.1 to 0.69 vol.% nanofiller. High electrical conductivity of 3.49 Sm$^{-1}$ was observed with 1.1 vol.% graphene contents. Nanoparticle dispersion formed conducting network in the matrix to improve the electrical conductivity values at percolation threshold. Furthermore, double-logarithmic plots of the polystyrene/graphene (0.33 vol.%) and polystyrene/carbon nanotube (0.50 vol.%) nanocomposites depicted values at 3.80 and 2.58, respectively. Transmission electron microscopy image of polystyrene/poly(lactic acid) blend showed two phase morphology. Graphene nanoparticles can be seen dispersed in the polystyrene matrix.

Poly (methyl methacrylate) and graphene based nanocomposites have been reported using the solution technique [59]. These nanomaterials have been studied for morphology, electrical conductivity, and mechanical characters [60]. The poly (methyl methacrylate) filled with 2.0 wt.% graphene contents had high electrical conductivity of 0.04 Sm$^{-1}$. Enhancement in electrical conductivity was attributed to the formation of interlinked graphene network in the matrix [61]. Polyethylene and graphene based nanocomposites were also formed using the solution method [62,63]. Similarly, poly(vinyl alcohol) and graphene based nanomaterials have been developed using solvent method [64]. Inclusion of 6.5 vol.% graphene to the matrix led to high conductivity of 0.06 Scm$^{-1}$. In addition, the Young’s modulus of poly(vinyl alcohol) was enhanced by 58 % [65]. Consequently, the low cost, simple, and ecofriendly solution technique has been applied on variety of thermoplastics and graphene nanofillers. The resulting high performance nanocomposites have superior dispersion, electrical and thermal conductivity, glass transition temperature, thermal stability, and mechanical strength performances [66,67].

5. Melt strategy for graphene nanocomposites

![Figure 6. Schematic of melt strategy.](image)

Melt strategy or melt extrusion technique has also been widely used for the
formation of polymer/graphene nanocomposites [68,69]. In this process, polymer as well as graphene are filled in an extruder using high temperature and shear rate conditions for melt processing (Figure 6). Melt technique has been used for better dispersal and chain alignment processes [70,71]. Commonly used polymers include polyamide matrices [72]. The polyamide 12 and graphene derived nanocomposites have been formed by melt compounding method [73]. Including 1.38 vol.% graphene loading enhanced the electrical conductivity to $6.7 \times 10^{-2}$ Sm$^{-1}$ [74].

Subsequently, numerous thermoplastic matrices have been melt processed with graphene nanoparticles [75]. Polystyrene and graphene based nanocomposites have been developed using melt blending [76,77]. These nanomaterials have revealed fine dispersion and electron conduction features. Shen and colleagues [78] industrialized the polystyrene and graphene derivatives nanocomposites through melt blending. Figure 7 shows a schematic for the development of $\pi-\pi$ stacking interactions in melt blending of polystyrene/graphene nanomaterials. Due to high shear forces, polymer chains are inserted between the graphene nanosheets. Figure 8 reveals the thermogravimetric analysis of the polystyrene/functional graphene nanocomposites. Inclusion of 5 to 60 wt.% nanofiller considerably boosted the thermal stability of the polystyrene matrix.

![Figure 7. Schematic for the formation of $\pi-\pi$ stacking during melt blending [78]. PS = polystyrene. Reproduced with permission from ACS.](image_url)

![Figure 8. Thermogravimetric analysis curves of nanocomposites. PSFG = polystyrene/functional graphene. 5, 10, 30, 60 = nanofiller contents in designations [78]. Reproduced with permission from ACS.](image_url)
The graphene filled polypropylene nanocomposites were processed using melt blending technique for enhanced electrical, thermal, and mechanical features [79]. The elevated performance was attributed to the interfacial interactions in the matrix-nanofiller [80]. Melt processed graphene filled polyethylene and polyethylene terephthalate nanocomposites have been developed with elevated strength features [81,82]. The poly(methyl methacrylate) nanocomposites with graphene have also been prepared through melt blending practice [83]. Melt strategy has been found facile, low cost, and large scale processable [84,85]. By controlling the reaction temperature, time, and shear and extrusion rate may define fine dispersion in the polymeric matrices [86,87].

6. More synthesis strategies

For graphene nanocomposites, solution approaches have been applied as effective methods, however, complex post treatments must be used for solvent evaporation [88]. Range of other synthesis strategies have been found effective for the formation of graphene nanocomposites. Essential processing techniques include three or four dimensional printing approaches [89]. Among printing methods, stereolithography [90], inkjet printing [91], selective laser sintering [92], direct ink writing [93], fused deposition modeling [94], and others have been used. Printing techniques have been used to enhance the dispersion as well as end properties and performances of the graphene nanomaterials [95,96]. Choice of a particular printing technique has been found critical to form the desired material and properties. Accordingly, the performance of printed material relies on the polymer type, nanoparticle dispersion, interactions, and printing parameters. The direct three dimensional printing involves the extrusion of viscous material from the pressurized syringe to form the three dimensional shapes. The fused deposition modeling printing performs with controlled filament extrusion. By controlling the printing parameters, product quality can be managed. The selective laser sintering uses high power lasers to fuse the powder and product resolution depends upon the powder specifications, laser power and scan speed. Electrospinning has also been adopted as an efficient and sophisticated method to form the high-tech nanomaterials [97,98]. By using electrospinning, finely reinforced graphene nanocomposites have been designed [98,99]. This technique may include a syringe, spinneret, collector, and voltage based system [100,101]. Resulting electrospun graphene nanocomposite nanofibers have been tested for high electrical, mechanical, thermal, and other advanced technical features [102]. Table 1 displays essential details of some literature reported graphene filled nanocomposite designs formed using the efficient synthesis strategies. Hence, the manufacturing technique relies on the inherent features of graphene nanomaterials.

<table>
<thead>
<tr>
<th>Matrices</th>
<th>Nanofiller</th>
<th>Manufacturing</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Polystyrene</td>
<td>Graphene</td>
<td>In situ polymerization</td>
<td>[35]</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>Graphene</td>
<td>In situ polymerization</td>
<td>[31]</td>
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<tr>
<td>Polystyrene</td>
<td>Graphene</td>
<td>Solution method</td>
<td>[56]</td>
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Table 1. (Continued).

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<tr>
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<td>Graphene</td>
<td>Solution method</td>
<td>[60]</td>
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<tr>
<td>Poly (methyl methacrylate)</td>
<td>Graphene</td>
<td>Solution method</td>
<td>[61]</td>
</tr>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>Graphene</td>
<td>Solution method</td>
<td>[64]</td>
</tr>
<tr>
<td>Polystyrene, polycarbonate, polypropylene, high density polyethylene</td>
<td>Graphene</td>
<td>Melt compounding</td>
<td>[75]</td>
</tr>
<tr>
<td>Poly (methyl methacrylate), polystyrene, polybutyl acylate</td>
<td>Graphene</td>
<td>Atom transfer radical polymerization</td>
<td>[103]</td>
</tr>
<tr>
<td>Polystyrene, poly (methyl methacrylate), poly (vinyl fluoride)</td>
<td>Graphene</td>
<td>Colloid method</td>
<td>[104]</td>
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7. Scenarios and conclusions

Graphene nanocomposites have been designed using several simple and sophisticated synthesis strategies (Figure 9) [105]. Choice of a particular technique always relies on the cost, ease of processing, and opportunities for the large scale production [106,107]. Accordingly, graphene dispersion, matrix-nanofiller interactions, and interface developments were influenced. Consequently, suitable synthesis technique has been found important to improve the nanocomposite features and end uses of the graphene nanocomposites [108]. Here, each synthesis method owns relevant advantages and disadvantages towards the formation of graphene nanomaterials [109].

![Figure 9. Synthesis strategies for graphene nanocomposites.](image)

Solution synthesis is a simple method; however, this may include drawback of using toxic solvent. The in situ technique, on the other hand, has resolved this issue by using environmental friendly solvents [110]. Melt method has also been found beneficial avoiding the use of any toxic solvent. Sometimes melt extrusion method may has drawback of poor graphene dispersion in the nanocomposites. Therefore, the nanofiller dispersion depends on the type of synthesis strategy used. Sophisticated techniques like printing and electrospinning have been found effective to form well dispersed high performance graphene nanocomposites [111]. However, these techniques have drawbacks of high cost and limitations for large scale processing [112,113]. Moreover, nanoparticle aggregation has been found challenging in sophisticated techniques like coating and plating [114]. Beside studying the
experimentally processed graphene nanocomposites, theoretical approaches like molecular dynamics or simulation must be applied for graphene nanomaterials [115]. Henceforth, research efforts have focused the use of appropriate synthesis techniques and controlled processing parameters to attain high performance graphene nanocomposites. Main application areas recognized for the well processed graphene nanocomposites include batteries, supercapacitors, solar cells, fuel cell, coatings, membranes, engineering structure, and space, automobile, and other transportation sectors.

In short, this article summarizes the synthesis strategies widely used for the formation of graphene nanocomposites. Most importantly, in situ strategy, solution processing, melt blending, printing, spinning and numerous other methods can be adopted for the development of efficient graphene filled nanomaterials. Here, opting suitable method may reveal fine graphene dispersion, matrix-nanofiller associations, and physical property enhancements. In this context, important microstructure, electrical, thermal, and mechanical features were improved with the graphene additions. Consequently, the nanocomposite performance was enhanced by controlling the parameters of synthesis strategies used. Future progress on the processing of graphene nanocomposites may lead to the development of advanced next level approaches for the formation of high-tech nanomaterials.

Conflict of interest: The authors declare no conflict of interest.

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