



Review

Manufacturing Strategies for Graphene Derivative Nanocomposites—Current Status and Fruitions

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Abstract: This review article highlights essential manufacturing strategies for the formation of graphene reinforced polymeric nanocomposites. For graphene reinforced thermoplastic, thermosetting and conducting matrix nanomaterials have been manufactured using solution casting, melt blending, in situ polymerization, electrospinning, 3D printing, and several other techniques. Solution processing has been well thought-out as an advantageous technique, relative to melt mixing, in terms of graphene dispersion in polymeric matrices. An in situ polymerization process has also been considered valuable to form homogeneously dispersed polymer/graphene nanocomposites having superior physical characteristics. Nevertheless, the manufacturing techniques for polymer/graphene nanocomposites have relative advantages and disadvantages to be considered for graphene-based nanocomposites. Moreover, numerous challenges need to be overcome to optimize the processing parameters for the fabrication of high-performance polymer/graphene nanocomposites.

Keywords: graphene; polymer; manufacturing; nanocomposite; solution casting; melt blending; in situ



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1. Introduction

The reinforcement of polymers with graphene has resulted in synergistic effects between the matrix and nanofiller that yield the high-performance polymer/graphene nanocomposite [1]. Here, important factors are the compatibility and processability of the polymer/graphene nanocomposites. Consequently, the optical, mechanical, thermal, and conducting properties of the nanocomposites rely on graphene dispersion in the matrix, or compatibilization effects with the polymer [2]. It has been observed that poor matrix–nanofiller miscibility may result in meager nanocomposite features. Therefore, manufacturing strategies have been focused on enhancing the interfacial interaction between the matrix and nanofiller [3]. Efficient processing techniques in turn may facilitate standardized nanocomposite structures and superior physical properties. In this regard, the polymer/graphene nanocomposites have been designed using facile approaches such as solution processing, melt blending, in situ polymerization, and other methodologies [4,5]. A range of polymeric matrices have been used with graphene including thermoplastic polymers (polystyrene, poly(methyl methacrylate), poly(vinyl chloride), poly(vinyl alcohol), polyethylene, poly(ethylene oxide), poly(vinyl fluoride), etc.), conducting polymers (polyaniline, polypyrrole, polythiophene, etc.), thermosetting polymers (epoxy), and rubbery

matrices. Some sophisticated manufacturing approaches such as electrospinning, 3D printing, lithography, etc. have also been used for the polymer/graphene nanocomposites. In these nanomaterials, both the weak physical forces [6] as well as the covalent linkages [7] may exist, depending upon the fabrication methodologies applied. Subsequently, a selection of manufacturing practices may cause better interfacial interactions between the polymers and graphene [8,9]. On the other hand, the poorly processed nanocomposites may have insolubility and intractability, so they cannot be employed for technical purposes [10].

This article offers a radical review on the aspects of manufacturing of polymer/graphene nanocomposites. To the best of our knowledge, this review is revolutionary for portraying the advancements in the manufacturing processes of graphene-based nanocomposites. Consequently, the formation of the nanocomposites using a polymer matrix, graphene, and the facile technique have been considered. The graphene nanofiller has been processed with several polymer matrices including poly(methyl methacrylate), polystyrene, polyethylene, polyamide, polyaniline, polypyrrole, and a number of other polymers. Accordingly, the ensuing polymer/graphene nanocomposites have been discussed under the categories of solution, melt, in situ, electrospinning, 3D printing, and other fabrication techniques, in this article. Then, the design, properties, and relevance of the nanocomposites are elaborated upon with respect to the fabrication methodologies. Towards the end, the significance of polymer/graphene nanomaterial manufacturing strategies, challenges, and future possibilities have been discussed. Thus, such a specific review on polymer/graphene nanocomposite manufacturing has not been seen in the literature before with well-arranged and well-conversed recent literature outlined. Henceforth, this review is groundbreaking for depicting the technical advancements in the field of polymer/graphene nanocomposite manufacturing. Despite the distinguished properties and potential of polymer/graphene nanomaterials, devoted future research efforts are still needed for the manufacturing techniques of high-performance nanocomposites, to overcome the associated challenges.

2. Graphene

Graphene is a one atom thick nanosheet consisting of sp^2 hybridized carbon atoms [11]. Graphene is a two-dimensional nanocarbon. It was initially discovered in 2004 [12]. Various synthesis approaches have been used to manufacture graphene including the mechanical cleavage of graphite, graphite exfoliation, chemical vapor deposition, and several organic synthesis approaches [13]. Graphene has unique structural and physical properties. Graphene is considered as the thinnest known material [14]. It has a Young's modulus of 1 TPa, which is 200 times stronger than steel [15]. The thermal conductivity and electron mobility of graphene are also found to be significantly high at $\sim 200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and 3000–5000 W/mK, respectively [16]. Graphene nanosheets have a tendency to wrinkle, due to weak van der Waals forces [17]. Consequently, graphene has been modified to create several functionalities on the surface. The most common type of functional graphene is graphene oxide having groups such as carbonyl, epoxide, hydroxyl, and carboxylic acid groups on the surface [18]. Figure 1 depicts the structures of graphene and graphene oxide. Graphene-based nanomaterials have been developed with high chemical stability, mechanical robustness, electrical/thermal conductivity, thermal constancy, etc. [19]. Especially, graphene nanofiller with polymer matrices have been exploited in energy devices [20], sensors [21], electronics [22], and membranes [23].

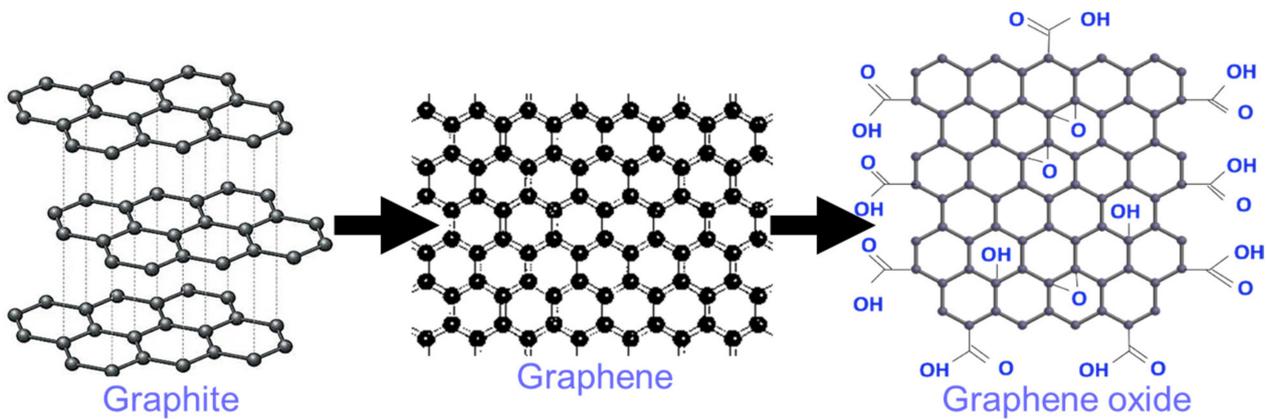


Figure 1. Graphite, graphene, and graphene oxide.

3. Polymer/Graphene Nanocomposite Manufacturing through Solution Mixing

Solvent casting or solution mixing is among the most common manufacturing techniques used for the formation of polymer/graphene nanocomposites [24]. This is an efficient and low-cost method used for polymer/graphene manufacturing. For this purpose, generally graphene nanosheets are dispersed in solvent. The polymer is also dissolved in solvent. Then, the two dispersions are mixed (Figure 2). The product is obtained through solvent evaporation. This solution method has been applied with a wide range of thermoplastic and thermosetting polymers [25]. Yu et al. [26] fabricated a polystyrene/graphene nanocomposite using a solution route and tetrahydrofuran solvent. Inclusion of a graphene nanofiller enhanced the thermal and mechanical properties of the nanocomposites. The glass transition temperature (T_g) of polystyrene was increased from 298 to 372 °C, with 2 wt.% graphene loading. With the same graphene content, the storage modulus revealed enhancement from 1808.8 to 2802.4 MP. He et al. [27] manufactured syndiotactic polystyrene and graphene-derived nanocomposites via solution blending. N-methyl-2-pyrrolidinone was used as a solvent. The effect of graphene inclusion on the electrical conductivity of the nanocomposite was explored. The polystyrene/graphene nanocomposite had an electrical conductivity of $1.5 \times 10^{-7} \text{ Sm}^{-1}$, with 10 wt.% nanofiller content. Mohammad-salih et al. [28] formed polystyrene and graphene oxide-derived nanocomposites through solution blending in a tetrahydrofuran solvent. For graphene dispersion, magnetic stirring and sonication were used. Fine graphene dispersal due to solution manufacturing positively affected the thermal and thermomechanical properties. Zhao and co-workers [29] synthesized polystyrene and graphene-based nanomaterials via a solution route. Morphological studies revealed fine interfacial adhesion between the matrix and nanofiller. With 0.957 vol.% graphene loading, a high electrical conductivity of 20.5 Sm^{-1} was attained. A percolation threshold of 0.0475 vol.% was observed.

Solution manufactured poly(methyl methacrylate)/graphene nanocomposites have also been found in the literature [30]. Zeng and co-researchers [31] designed a poly(methyl methacrylate)/graphene nanocomposite using a solution blending technique. The poly(methyl methacrylate)/graphene nanocomposite revealed an increase in electrical conductivity due to graphene interlinking in the percolation network. As displayed in Figure 3, the electrical conductivity continuously increased with the nanofiller content. A high electrical conductivity of 0.037 Sm^{-1} was attained with 2.0 wt.% nanofiller addition. The T_g of the nanocomposites also improved with the increase in the graphene content. Balasubramaniyan et al. [32] also prepared a poly(methyl methacrylate)/graphene nanocomposite via the solution method in dimethylformamide solvent. The electrical conductivity of the nanocomposites was enhanced up to 0.039 Sm^{-1} . Moreover, enhancements of the T_g and storage modulus of the nanocomposites were found with the addition of graphene.

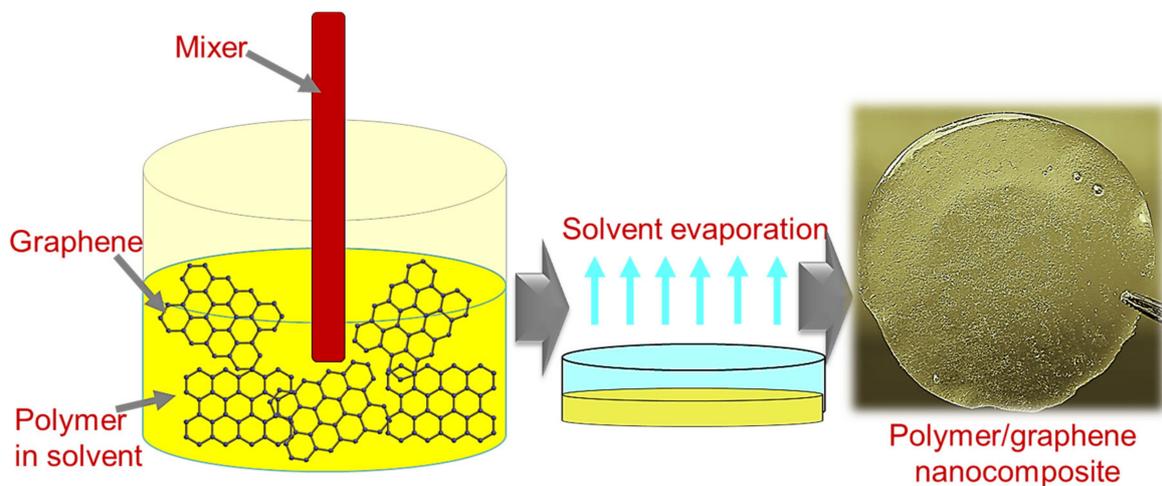


Figure 2. Solution mixing set-up.

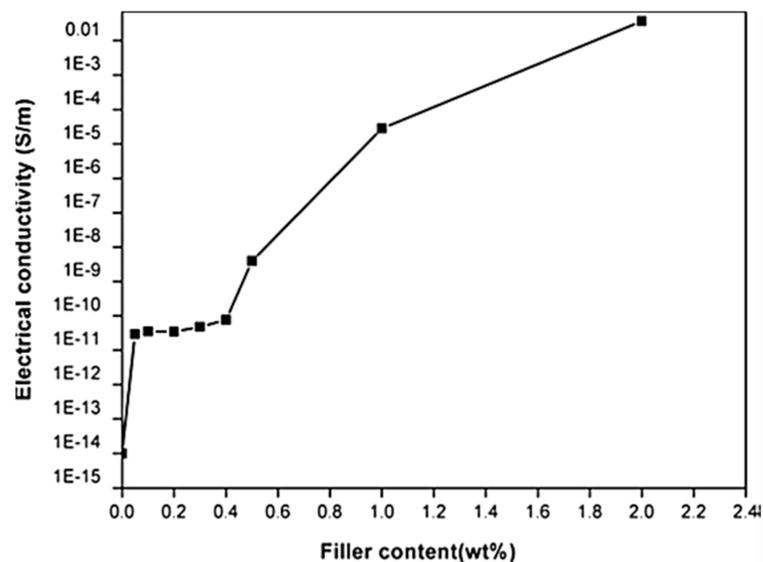


Figure 3. Electrical conductivities as a function of nanofiller content [31]. Reproduced with permission from Elsevier.

Solution manufacturing has also been applied to polyethylene/graphene nanomaterials. Consequently, Kuila et al. [33] considered solution processing for manufacturing polyethylene/graphene nanocomposites in a xylene solvent. According to their morphological studies, the graphene developed uniform dispersal in a polymer matrix due to interfacial interactions between the matrix and graphene. In a poly(vinyl alcohol) matrix, graphene has been dispersed using a solution technique by Vadukumpully et al. [34]. Dimethyl formamide was used as solvent. In poly(vinyl alcohol), the addition of 6.47 vol.% graphene resulted in an electrical conductivity of 0.058 Scm^{-1} . The tensile strength and Young's modulus of the poly(vinyl alcohol)/graphene nanocomposite was enhanced by 130% and 58%, respectively, with 2 wt.% reinforcement. Epoxy has also been filled with a graphene nanofiller using the solution route [35]. Yao et al. [36] reported on a solution-processed epoxy/graphene nanocomposite. An amount of 5 wt.% finely dispersed graphene nanosheets enhanced the thermal conductivity up to 0.56 W/mK [37].

In conducting polymeric matrices, graphene nanofiller has been filled via a solution manufacturing route [38]. Commonly, polyaniline [39], polypyrrole [40], polythiophene [41], etc. and graphene have been formed through solution mixing. In styrene-butadiene-rubber, graphene was filled using solution manufacturing by Araby et al. [42].

Melt blending was also applied to develop the styrene-butadiene-rubber/graphene nanocomposites. The 10.5 vol% filled styrene-butadiene-rubber/graphene nanocomposites were formed using both the solution and melt routes. The tensile strength, Young's modulus, and tear strength of solution-manufactured nanocomposites reveal an enhancement of 390%, 580%, and 500%, respectively, relative to the melt-processed nanocomposites with increases of 137%, 145%, and 193%, correspondingly (Figure 4).

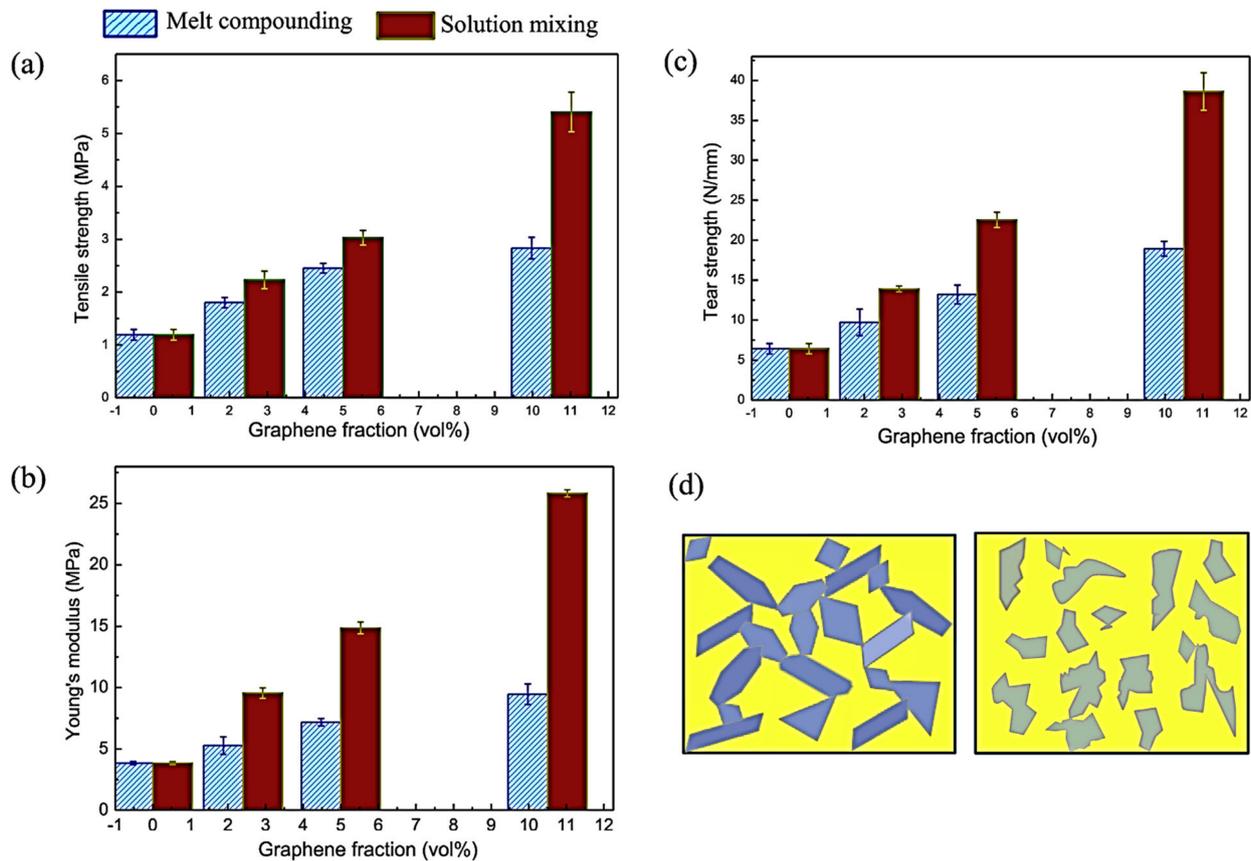


Figure 4. Solution mixing vs. melt compounding: (a) tensile strength; (b) Young's modulus; (c) tear strength; and (d) schematic of nanocomposites by solution compounding (left) and melt mixing (right) [42]. Reproduced with permission from Elsevier.

It was suggested that high shear force and temperature in melt compounding may damage the lateral dimensions of graphene and its resulting dispersion. Therefore, solution manufacturing was adopted as a facile method to enhance the mechanical features of the nanocomposites.

In addition, the polymer/graphene manufacturing through solution mixing has positively affected the dispersion, electrical conductivity, thermal conductivity, glass transition temperature, thermal stability, and mechanical performance of the nanomaterials [43]. The solution route has undoubtedly led to the formation of fine interfacial interactions in polymer/graphene nanomaterials, leading to enhanced physical properties. Due to the adsorption of the organic solvent between the graphene layers, the wrinkling of graphene nanosheets is avoided to enhance the dispersion [44,45]. The solvent adsorption on graphene nanosheets has been observed using spectroscopic and elemental analysis techniques [46,47]. Graphene oxide reveals a greater propensity to adsorb moisture owing to surface functionalities, relative to neat graphene [48]. Polar aprotic solvents such as N,N-dimethylformamide dimethyl sulfoxide, acetone, etc. [49], and chloride solvents such as chloroform, carbon tetrachloride, etc. [50] have been found to be retained between the graphene layers. Despite the benefits of solution manufacturing, due to the

use of environmentally harmful organic solvents, this method has not been recommended for large-scale productions.

4. Melt Blending for Polymer/Graphene Nanocomposite Manufacturing

Melt blending has been considered as a superlative manufacturing technique for the polymer/graphene nanocomposites [51,52]. This is a straightforward method to combine the polymer and graphene. The desired components are fed into an extruder. High shear rate and temperature conditions are applied during melt processing. A simple melt compounding set-up is given in Figure 5. Numerous melt cast polymer/graphene nanocomposites have been prepared and explored for Various polyamide matrices have been melt-processed in the presence of graphene nanosheets [53]. The dispersion properties of the nanocomposites were studied. nanosheet dispersion, polymer chain confinements, and nanocomposite features [54].

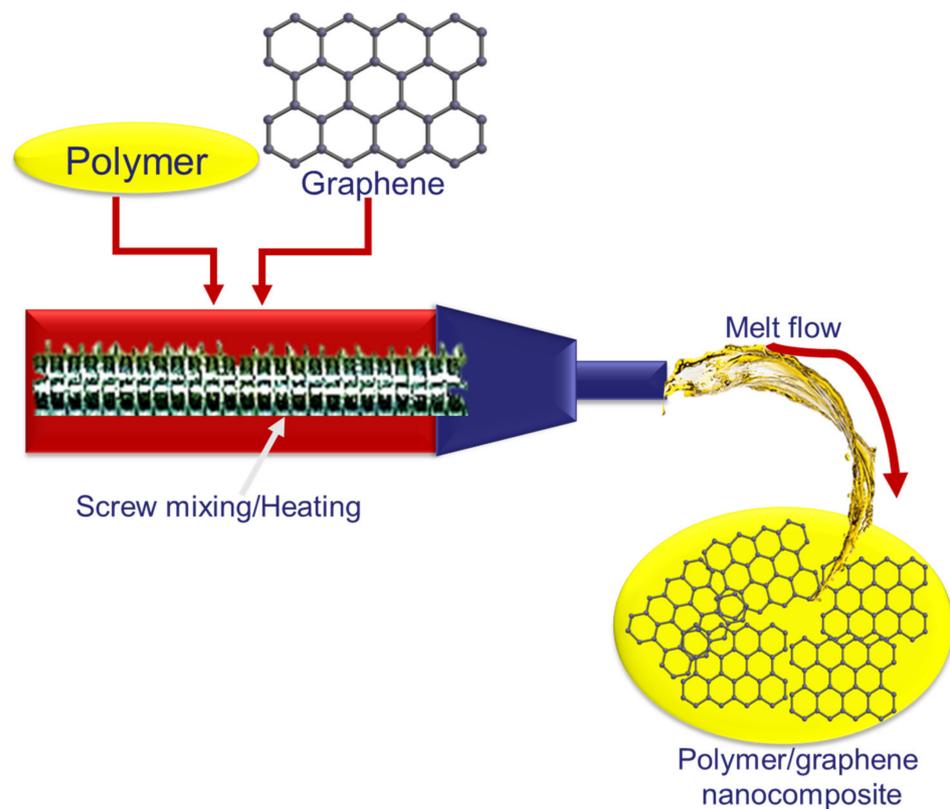


Figure 5. Melt compounding set-up of polymer/graphene nanocomposite.

Yan and co-workers [55] manufactured the polyamide 12/graphene nanocomposites via melt compounding. At 1.38 vol.% graphene loading, the electrical conductivity of polyamide 12 was enhanced from $\sim 2.8 \times 10^{-14}$ to $6.7 \times 10^{-2} \text{ Sm}^{-1}$. Kausar [56] formed polyamide1010/graphene nanomaterials. The mechanical, thermal, and non-flammability properties were improved with the graphene loading.

Consequently, graphene has been melt-processed with a number of thermoplastic matrices such as polystyrene, polypropylene, polycarbonate, high density polyethylene, linear low density polyethylene, etc. [57]. Shen et al. [58] manufactured melt blended polystyrene/graphene nanocomposites. The nanomaterial had uniform dispersion and improved electrical properties. Shen et al. [59] developed polystyrene- and functional graphene-based nanocomposites using melt blending. Figure 6 shows the shear mixing of polystyrene, graphene, and π - π stacking interaction development during melt blending. The formation of π - π interactions led to enhanced matrix-nanofiller compatibility and thermal stability. The thermogravimetric analysis curves of the polystyrene/functional

graphene nanocomposites are given in Figure 7. The effect of 5–60 wt.% graphene loading was observed on the thermal stability of the nanocomposites. High thermal stability was observed at 5 wt.% graphene reinforcement, due to better nanofiller dispersion. However, higher graphene loading led to nanofiller aggregation and deterioration of the thermal properties of the nanocomposites.

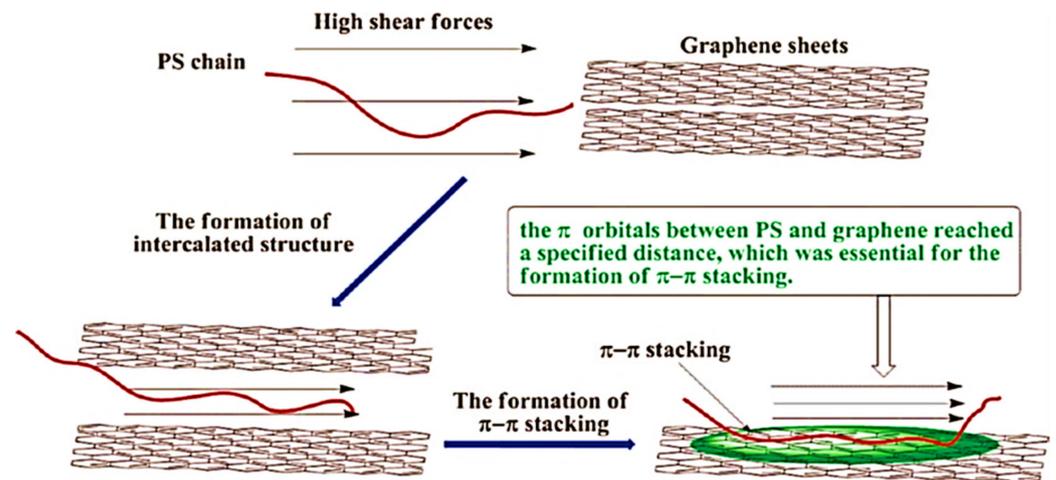


Figure 6. Schematic for the formation of π - π stacking during melt blending [59]. PS = polystyrene. Reproduced with permission from ACS.

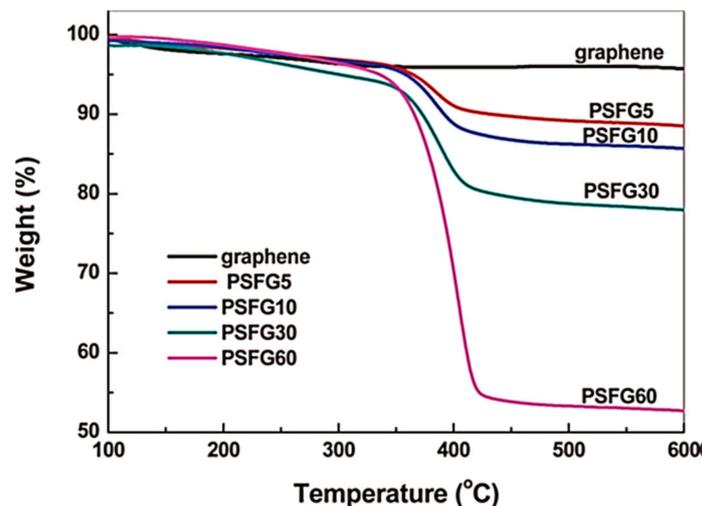


Figure 7. Thermogravimetric analysis curves of nanocomposites. PSFG = polystyrene/functional graphene. The values 5, 10, 30, 60 = nanofiller contents in designations [59]. Reproduced with permission from ACS.

Achaby et al. [60] produced a polypropylene/graphene nanocomposite through melt blending with superior mechanical and thermal properties. The interfacial interactions in melt-processed polypropylene/graphene nanocomposites have been studied [61]. Istrate et al. [62] prepared melt-processed polyethylene terephthalate/graphene nanocomposite. The 0.07 wt.% graphene content led to an improved tensile strength of 40%, relative to the neat polymer. Maiti et al. [63] also used the melt technique to form the polyethylene terephthalate/graphene nanocomposite. Jiang and co-workers [64] produced a poly(methyl methacrylate)/graphene nanocomposite via the melt technique. The compatibility and interfacial interactions between the matrix and graphene have been studied. Ansari et al. [65] reported on poly(vinyl fluoride) and graphene nanosheet nanocompos-

ites with the melt route. The storage modulus of the nanocomposites improved with the addition of graphene contents.

Subsequently, melt blending has been adopted for the formation of several thermoplastic polymer/graphene nanomaterials [66]. It has been adopted as an ecofriendly, low cost, and large-scale production technique [67–69]. Moreover, the melt parameters such as temperature, blending time, shear rate, and extruder speed can be easily monitored [70]. Though, poor graphene dispersion has been considered as a major disadvantage of this technique [71]. Poor dispersion may result in the low mechanical performance of the nanocomposite [72].

5. In Situ Polymerization to Form Polymer/Graphene Nanocomposites

In situ polymerization has been adopted as an efficient manufacturing technique to better disperse graphene nanosheets and develop physical and chemical interactions in the matrix–nanofiller [73]. This method employs non-toxic environment-friendly solvents and materials while processing. Various polymers have been in situ polymerized in the solvents with graphene nanofiller [74]. The styrene monomer has been in situ polymerized in the presence of graphene nanosheets [75]. During this process, usually a styrene monomer is dispersed in a surfactant and graphene mixture. The styrene monomers first get adsorbed on the graphene nanosheet surface, and then in situ polymerized. In some cases, first the in situ polymerized polystyrene microparticles are produced and then they interact with the graphene nanosheets [76,77]. The in situ polymerization frequently led to better interactions and compatibility in the polystyrene/graphene nanocomposites [78]. The in situ manufactured nanocomposites revealed enhanced electrical conductivity, glass transition temperature, and thermal stability features [79]. Tu et al. [80] manufactured polystyrene/graphene and polystyrene/graphene oxide nanocomposites using an in situ method. Here, hexadecyl trimethyl ammonium bromide was used as the initiator/surfactant. Electrostatic interactions developed between the polystyrene dispersion and charged graphene oxide nanosheets (Figure 8). The polystyrene/graphene oxide nanocomposite was converted to polystyrene/graphene nanomaterial through in situ reduction. Transmission electron microscopy exposed the morphological features of polystyrene dispersion, polystyrene/graphene, and polystyrene/graphene oxide nanocomposites. Figure 9 displays homogeneous polystyrene nanoparticles with a diameter of ~130 nm. The graphene oxide or graphene nanosheets can be observed scattered between the polystyrene phases. The nanosheets seem to interconnect the polymer particles to create a continuous structure. The better-connected continuous polymer/graphene network in turn affected the nanocomposite properties. In the polystyrene/graphene nanocomposite, the graphene nanosheets developed a network to promote electron conduction. Consequently, the nanocomposite with 1.53 vol.% loading revealed a high electrical conductivity of 46.32 Sm^{-1} . The thermal conductivity of the polymer/graphene nanocomposites also increased with the increasing nanofiller contents. At 1.53 vol.% graphene loading content, the nanocomposite had a thermal conductivity 0.47 W/mk (Table 1).

Polyamide 6 nanocomposites have been formed via in situ polymerization of a ϵ -caprolactam monomer [81]. During the process, 1.64 vol.% graphene was added. The in situ generated polyamide 6/graphene nanocomposite had an electrical conductivity of $\sim 0.028 \text{ Sm}^{-1}$. Ding and co-researchers [82] developed the polyamide 6/graphene nanocomposite using an in situ method. The thermal conductivity of polyamide 6/graphene nanocomposite was enhanced up to $0.265 \text{ Wm}^{-1}\text{K}^{-1}$. Chen et al. [83] manufactured the in situ generated polyamide 6/graphene oxide nanocomposite. Here, the graphene oxide loading improved the thermal conductivity of the nylon matrix. Xu et al. [84] studied the in situ polymerization of ϵ -caprolactam in the presence of graphene oxide. The polyamide 6/graphene nanocomposites were explored for their mechanical properties. The polymerization of the ϵ -caprolactam monomer on functional graphene surfaces caused the formation of compatible nanocomposites. Compared with the neat nylon, inclusion of

0.1 wt.% graphene oxide loading led to an increase in tensile strength and Young's modulus by 2.1 and 2.4 folds, respectively.

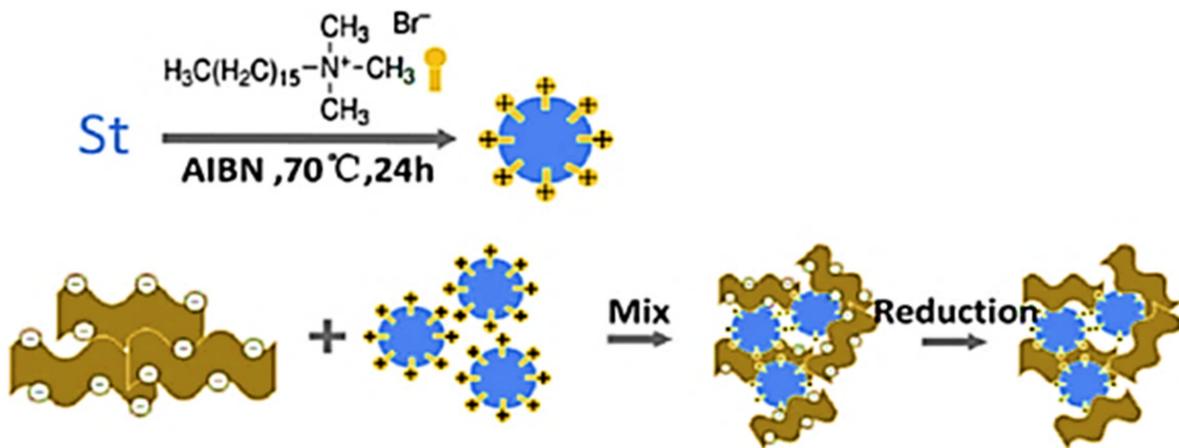


Figure 8. Schematic of fabrication of the polystyrene/graphene nanocomposite [80]. Reproduced with permission from Elsevier.

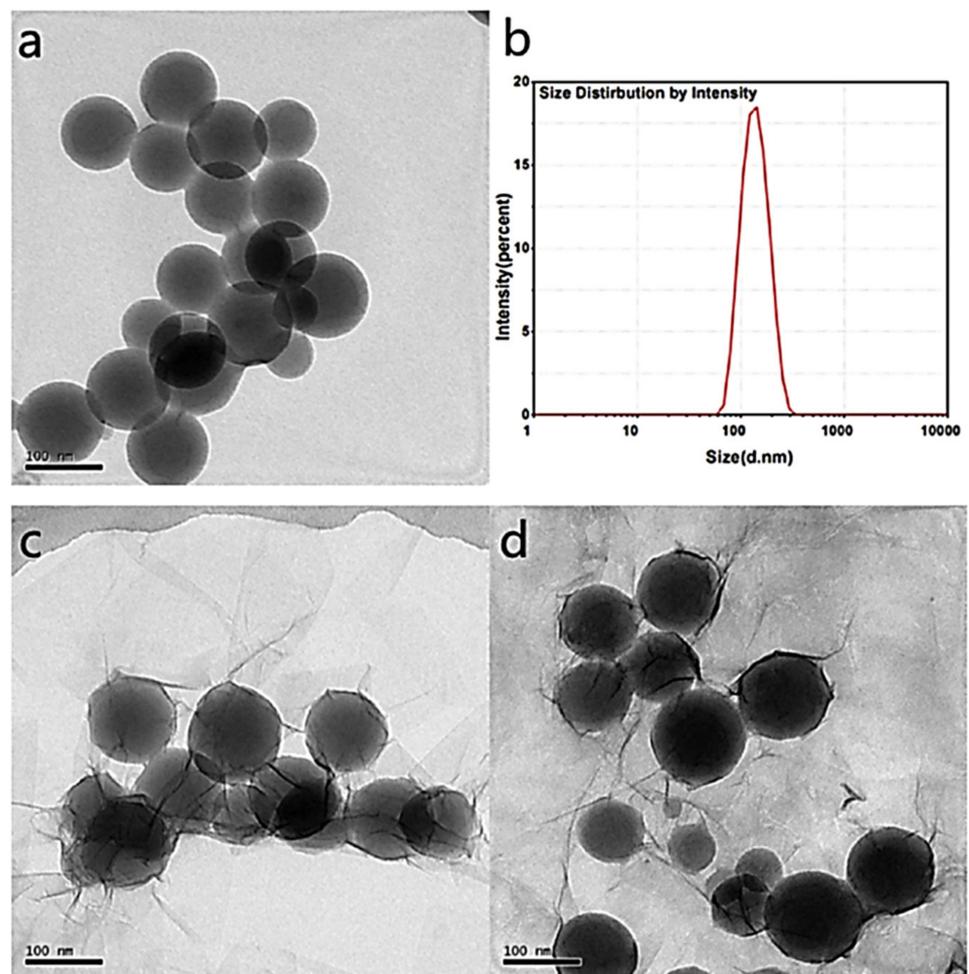


Figure 9. (a) Transmission electron microscopy images of polystyrene dispersion; (b) size distribution of polystyrene microspheres; (c) polystyrene nanocomposite with 1.34 vol.% graphene oxide before in situ reduction, and (d) polystyrene/graphene nanocomposite with 1.34 vol.% graphene [80]. Reproduced with permission from Elsevier.

Table 1. Thermal conductivity of polystyrene/graphene nanocomposites with different nanofiller contents [80]. Reproduced with permission from Elsevier.

Graphene concentration (vol.%)	0.00	0.01	0.05	0.81	1.53
Thermal conductivity (W/mK)	0.16	0.16	0.18	0.36	0.47

Wang et al. [85] manufactured the poly(methyl methacrylate)/graphene nanocomposite through in situ polymerization. The covalent interactions between the poly(methyl methacrylate) chains and graphene were studied. Lee et al. [86] used the in situ method on waterborne polyurethane and graphene nanosheets. Better electrical conductivity due to a low percolation threshold (0.078 vol.%) was observed in the polyurethane/graphene nanocomposite. This reason was attributed to the interfacial interaction developed between the matrix and nanofiller during processing [87,88].

In addition to thermoplastic polymers, conducting polymers have been used to form the nanocomposites with graphene [89,90]. Abdullah et al. [91] formed polyaniline/graphene nanocomposites through in situ polymerization. Figure 10 shows the development and interactions between the polyaniline and graphene nanosheets.

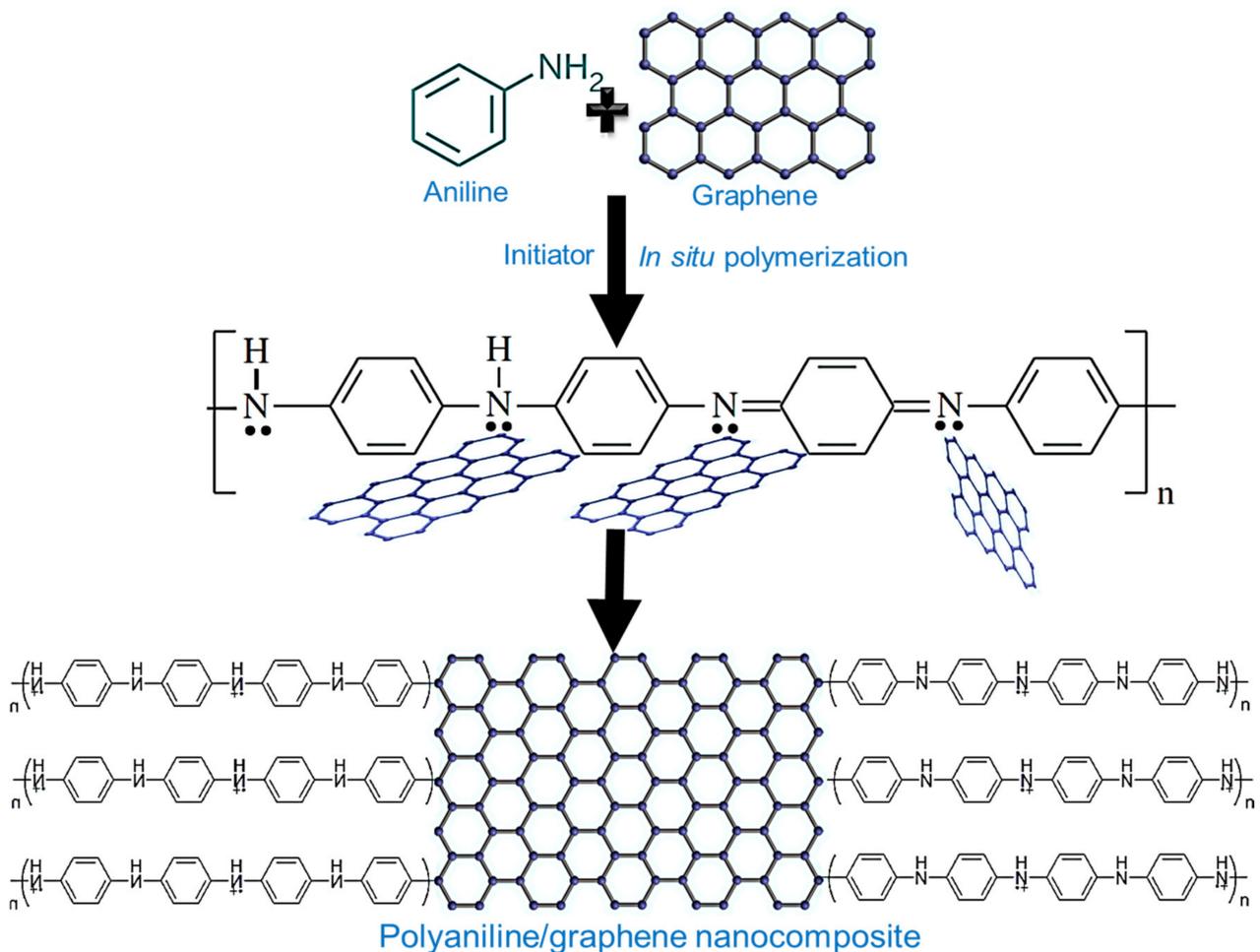


Figure 10. In situ polyaniline/graphene nanocomposite.

The aniline monomer was polymerized with 0.1–10 wt.% graphene contents. With the nanofiller loading during in situ manufacturing, D.C. conductivity was varied in the range of 1.66–186.57. Manna et al. [92] also reported on in situ polyaniline/graphene nanocomposites. The fine graphene dispersion and interaction with polyaniline led to better electrical conductivity and a high electromagnetic shielding of 65 dB. Thus, the

in situ polymerization technique has been considered important to better develop physical/covalent linking between the polymer and graphene nanosheets [93]. Nevertheless, this technique has a key drawback of there being an increase in the viscosity of the medium during polymerization. Despite the shortcomings, in situ polymerization has been used to form various well-processed polymer/graphene nanocomposites [94].

6. Electrospinning Technique

Electrospinning has been considered as a sophisticated manufacturing technique for polymeric nanocomposites [95]. The material is generally produced in the form of nanofibers. Graphene-filled polymeric nanocomposite nanofibers have been produced using electrospinning [96]. The electrospinning has been carried out using a set-up with a syringe with polymer/graphene dispersion, a spinneret, a collector, and a high-voltage system [97]. During nanofiber spinning, the polymer solution is fed into a syringe with a needle. The polymer solution ejected from the needle forms a fiber jet under an applied voltage [98]. Due to the electrostatic driving force, the nanofibers move to the spinneret and collector. Due to the electrostatic field, fine nanofibers have been generated using various materials [99–101]. The electrospinning parameters have been adjusted to better regulate the resulting electrospun fiber texture, microstructure, and physical characteristics. The electrospun polymer/graphene nanofibers have upgraded electrical, thermal, and mechanical properties, relative to neat polymer nanofibers and non-electrospun nanocomposites [102]. Transmission electron microscopy and scanning electron microscopy have been mostly adopted to study the nanofiber morphology. Consequently, the electrospinning technique has been predictable as a fast and competent method for manufacturing polymer/graphene nanofibers [103]. Consequently, the high performance electrospun polymer/graphene nanocomposite nanofibers have been pragmatic in energy devices, sensors, membranes, tissue engineering, etc. [104]. As a suggestion, electrospinning can be combined with the solution, melt, and in situ techniques to improve efficiency of these methods, and also to overcome their related drawbacks [105]. The formation of advanced electrospun polymer/graphene nanofibers has highlighted the significance of the electrospinning technique for technical fields.

7. The 3D Printing of Polymeric/Graphene Nanocomposites

Three-dimensional printing skills have been developed over the past years [106]. These technologies may employ a thermoplastic polymer, nanoparticles, metals, etc. The graphene nanomaterials derived from 3D printed materials have been sought for advanced features and processing [107]. Three-dimensional printing is a manufacturing method useful for printing 3D objects through appropriated ways. The precise deposition of printable material is required for fine 3D printing. One important technique involves the layered deposition, referred to as additive manufacturing. The 3D structure is usually created with processes such as milling, drilling, sawing, broaching, etc. The selection of printable material, cost, morphology, structural intricacy, and the manufacturing practices define the final product quality. Moreover, the structural geometry relies on the complexity of 3D manufacturing techniques. Graphene nanocomposites have been developed using 3D printing approaches such as inkjet 3D printing [108], direct ink writing [109], selective laser sintering [110], stereolithography [111], fused deposition modeling [112], etc. The properties and end performance of the 3D printed polymer/graphene depends on the type of polymer matrix, graphene dispersion, graphene functionality, matrix–nanofiller interaction, and printing parameters. Studies have been performed on the electrical, thermal, mechanical, and other physical characteristics of 3D printed graphene nanomaterials to explore the potential of this manufacturing technique [113]. Although 3D printing is a sophisticated technique, it has been less explored for polymer/graphene nanomaterials due to process limitations. The 3D printed graphene nanomaterials have found application in strain sensors, wearable electronic sensor devices, and electrochemical sensors [114]. Moreover, the 3D printed graphene nanocomposites have been applied in high temperature materials,

supercapacitors, solar cell, batteries, etc. Thus, 3D printed graphene nanocomposites have wide ranging technical applications [115–117].

8. Other Manufacturing Practices

Despite all of the above-mentioned manufacturing techniques, several other methods have also been adopted to form polymer/graphene nanocomposites. For example, interfacial polymerization has been used for manufacturing polyaniline/graphene nanocomposites [118]. However, this method has been relatively less explored for the polymer/graphene nanocomposites. For better polymer/graphene interactions via π - π stacking, or physical/chemical means, the atom transfer radical polymerization [119], reversible addition fragmentation chain transfer [120], Ziegler–Natta polymerization [121], and frontal polymerization [122] have been applied to form the polymer/graphene nanomaterials. The polypropylene, polystyrene, poly(vinyl fluoride), poly(methyl methacrylate), etc. with graphene nanofiller have been processed via bulk polymerization, microwave irradiation, colloidal practice, latex technology, and cryomilling [123–125]. The colloid and latex methods have been used to obtain consistently dispersed nanocomposites. Another efficient technique is layer-by-layer assembly to control the morphology and physical properties of the polymer/graphene nanomaterials [126,127]. Among all techniques, manufacturing methods with a low cost, high yield, and easy parameter optimization have been preferred. The selection of appropriate processing methods may lead to enhanced structural and functional characteristics of the nanocomposites. Table 2 demonstrates a summary of nanocomposite systems and manufacturing methods applied.

Table 2. Specifications of polymer/graphene nanocomposites using various manufacturing strategies.

Matrices	Nanofiller	Manufacturing	Ref.
Polystyrene	Graphene	Solution method	[26]
Poly(methyl methacrylate)	Graphene	Solution method	[31]
Poly(methyl methacrylate)	Graphene	Solution method	[32]
Polyethylene	Graphene	Solution method	[33]
Poly(vinyl alcohol)	Graphene	Solution method	[34]
Epoxy	Graphene	Solution method	[36]
Polystyrene, polycarbonate, polypropylene, high density polyethylene, low density polyethylene	Graphene	Melt compounding	[57]
Polystyrene	Graphene	In situ polymerization	[75]
Polyamide 6	Graphene	In situ polymerization	[83]
Polyamide 6	Graphene	In situ polymerization	[82]
Poly(methyl methacrylate)	Graphene	In situ polymerization	[85]
Waterborne polyurethane	Graphene	In situ polymerization	[86]
Polyaniline	Graphene	Interfacial polymerization	[118]
Poly(methyl methacrylate), polystyrene, polybutyl acrylate	Graphene	Atom transfer radical polymerization	[119]
Polypropylene	Graphene	Ziegler–Natta polymerization	[121]
Poly(N-isopropylacrylamide)	Graphene	Frontal polymerization	[122]
Poly(methyl methacrylate)	Graphene	Microwave irradiation	[123]
Polystyrene, poly(methyl methacrylate), poly(vinyl fluoride)	Graphene	Colloid method	[125]

9. Significance and Summary

The performance of polymer/graphene nanocomposites produced by the above surveyed manufacturing techniques relies on the graphene contents, graphene functionality, dispersion, matrix–nanofiller interactions, interface formation, etc. [128]. All these features of polymer/graphene nanocomposites have been found dependent on the processing technique used and the related parameters. Figure 11 shows various technical areas of the polymer/graphene nanocomposites processed by solution, melt, in situ, electrospinning, 3D printing, latex, colloidal, microwave, layer-by-layer, and other manufacturing techniques. The major application areas identified for the manufactured polymer/graphene nanocomposites include solar cells, fuel cells, supercapacitors, batteries, membranes, coatings, etc. in addition to the aerospace, automotive, and civil sectors.

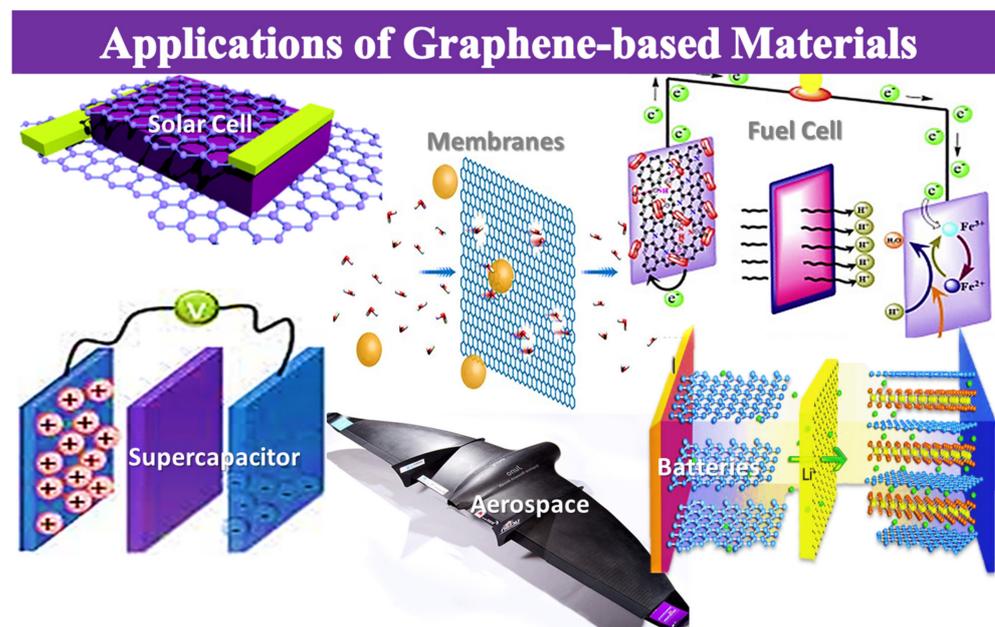


Figure 11. Applications of polymer/graphene nanocomposites.

The graphene nanosheet dispersion and nanocomposite morphology contribute to enhanced properties of the nanocomposites. The nanofiller scattering and ensuing microstructure of the nanomaterials strongly depend on the manufacturing technique used. The manufacturing parameters in fact determine the extent of nanofiller dispersion in the polymers. Despite the disadvantage of using noxious solvents in solution mixing, the morphology of the manufactured nanocomposites through this route has been observed as homogeneous, relative to the melt-processed systems. The in situ technique has also been successfully used to enhance nanomaterial consistency, although it possesses processing shortcomings [129]. Electrospinning has been used as an efficient technique, however applicable only to attain the nanofiber end-products. Nevertheless, it is still challenging to achieve unvarying graphene dispersion in the polymeric matrices using a single technique, and have all the controlled parameters including eco-friendliness. Thus, the development of modified techniques for high performance nanocomposite manufacturing is desirable. The major shortcoming of nanofiller aggregation in polymer matrices has been identified as the formation of non-consistent phase-separated structures [130]. These may sequentially decrease the mechanical interlocking and interfacial bonding between the polymer chains and graphene nanosheets. Therefore, the overall physical properties of the non-homogeneous polymer/graphene nanocomposite may seriously decline. In this regard, the functionalities on the graphene surface not only enhance interactions with polymers, but also promote the formation of a conducting network and interlinked structure, leading to the load transfer properties. Thus, the functional graphene nanosheets processed through

appropriate manufacturing strategies may form aligned and homogeneous microstructures in the polymer/graphene nanomaterials. Both the physical and covalent bonding may form between the functional graphene nanosheets and the polymer matrix. It is suggested that the covalent bonding in the matrix–nanofiller better prevents graphene accumulation due to fine adhesion at the interface. Molecular dynamics and molecular simulation studies must be carried out to further understand the structure and interactions in the polymer and graphene-derived nanomaterials [131].

Briefly speaking, numerous manufacturing strategies have been applied to form the polymer/graphene nanocomposites. Common methods used are solution casting, melt blending, in situ polymerization, electrospinning, interfacial polymerization, the latex/colloidal method, microwave irradiation, the layer-by-layer method, and several other manufacturing methods. The choice of the right manufacturing method directly influences the nanocomposite microstructure and electrical, mechanical, thermal, and physical properties of these polymer/graphene nanocomposites. However, each technique has relative advantages and disadvantages which need to be considered before fabrication. Solution mixing causes homogeneous graphene dispersion, although it may cause environmental noxiousness. Melt compounding has been found advantageous, however, poor graphene dispersion may occur due to the extreme shear/temperature conditions. The in situ method may result in fine graphene dispersal, but it has the shortcoming of being non-effective for large scale manufacturing. Therefore, the selected manufacturing technique must result in uniform dispersion, uniform morphology, superior physical properties, high yield, and low eco hazards. Hence, these research advancements have been found desirable for comprehending the processing parameters of existing techniques, and for the development of novel manufacturing methods to form polymer/graphene nanocomposites.

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