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Review

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Advancements in Graphene-Based Hybrid Filler Polymer Composites: A Comprehensive Survey of Processing, Properties, and Influential Factors

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Abstract: The escalating demand for multifunctional and advanced materials for growing industries has turned scientific exploration to graphene-based hybrid filler polymer composites. The introduction of graphene with other fillers into polymer matrices results in astonishing properties and thus has gained significant attention in recent years. This study addresses the significance of graphene-based hybrid filler polymer composites in progressive materials science and engineering. The paper encloses some traditional and current preparation techniques employed in the fabrication of composites and a comprehensive review of successfully prepared graphene hybrid polymer composites with enhanced mechanical, thermal, and electrical properties reported in published research. The role of different factors, e.g., filler type, aspect ratios, filler-matrix compatibility, dispersion effects, homogeneity, filler orientation through polymer matrices, and curing conditions, are summarized. Finally, the applications in heavy industries, e.g., aerospace, electronics, energy storage, and automotive sectors were also analyzed. We hope this study will serve as a practical resource for new researchers and practitioners to understand and harness the full potential of these composites in various scientific and industrial fields.

Keywords: graphene; polymers; hybrid composites; properties; influencing factors; applications

1. Introduction

The demand for hybrid filler polymer composites has substantially enhanced through multifunctional devices, highly integrated circuits, and heavy industries due to unique properties governed by the amalgamation of cutting-edge materials that fulfill the requirements of modern industrial applications [1]. Incorporating hybrid filler polymer composites, using carbon fillers like graphene, carbon nanotubes, carbon fibers, and nanoparticles, provides synergistically enhanced interconnected structures with high mechanical strength, thermal and electrical conductivity, and barrier properties. Hybrid polymer composites find many applications in next-generation technologies, ranging from robust and lightweight aerospace components to energy-efficient wind turbine blades and high-performance electronic devices with flexible models [2–4].

Graphene, a two-dimensional arrangement of carbon atoms, offers excellent properties to incorporate polymer composites. Due to the high specific surface area (2600 m^2g^{-1}), graphene establishes excellent combination with other fillers and polymer matrices, facilitating effective stress distribution and support within the composite structure. Adding graphene with carbon nanotubes, nanoparticles, carbon fibers, and natural fibers presents an intense interplay with great potential for multifunctional materials that reshape heavy industries [5–7]. In 3D connected structured hybrid

polymer composites, the presence of graphene highly induces mechanical, thermal, and electrical properties due to its intrinsic high mechanical strength, higher Young's modulus ~1 TPa, high thermal conductivity (~5000 $Wm^{-1}K^{-1}$), and high electrical conductivity (~$6.6x10^6$ Sm^{-1}). Owing to fascinating properties, graphene-based polymer composites find applications [8] in various fields such as heat dissipation [9], membranes, flexible sensors [10], encompassing electronics [11], actuators, anti-corrosion coatings, thermal insulators, military, and firefighting materials. Moreover, these composites can be utilized in aerodynamic-enhanced designs for aerospace vehicles with reduced drag, promoting aerodynamic efficiency [12,13]. Figure 1 explains the general outline of this review paper.
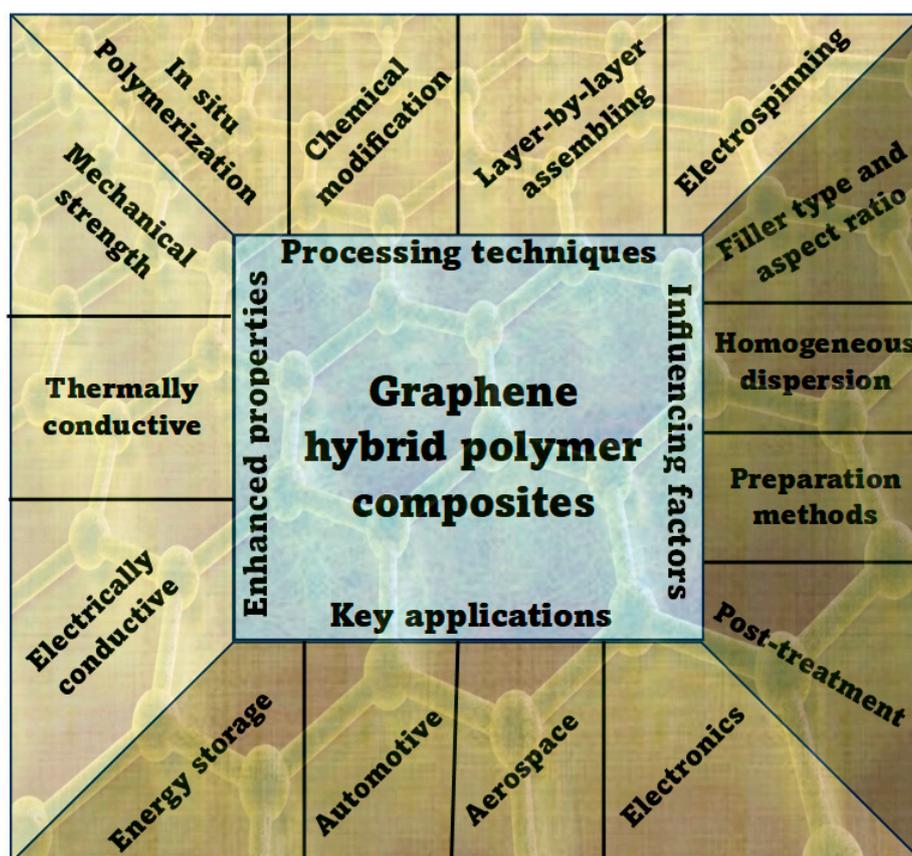

Figure 1. Reviewed key aspects of graphene hybrid polymer composites in this literature.

This study summarized different aspects of graphene-based hybrid filler polymer composites, including the traditional and recent processing techniques, a deep insight into successfully prepared composites reported in different literatures, and mechanical, thermal, and electrical properties. Furthermore, the properties influencing factors and applications in different sectors were enclosed. Finally, the conclusion and future perspectives were also analyzed.

2. Processing Techniques

2.1. Old Preparation Methods for Graphene and Hybrid Polymer Composites

2.1.1. Mechanical Mixing

Mechanical mixing is a conventional method used to fabricate graphene-based hybrid polymer composites. This method uses mechanical forces, e.g., high-speed mixers, ball mills, mortar, and pestle, to get a homogeneous mixture of graphene and other fillers with a polymer matrix. However, this method is beneficial due to its low cost, scalability, and suitability for different polymer matrices, but irregular dispersion and high filler loading cause agglomeration to be a bottleneck. Thus,

additional methods, e.g., sonication or surface modification, can be adopted to improve dispersion efficacy [15–17]. Jing et al. [18] developed graphene nanoplatelets (GNPs) coated Linear low-density polyethylene (LLDPE) nanocomposites with permeable and complex geometry using a ball-milling technique. The LLDPE/GNPs composite presented superb electromagnetic interference shielding effectiveness (EMI-SE) of ~32.4 dB with a customizable and optimized structure. Awasthi et al. [19] produced porous Molybdenum disulfide nanoparticles (MoS_2) linked with thin layered reduced graphene oxide (rGO) by ultrasonic chemical method for supercapacitor applications and it was observed that rGO increased the surface area and conductivity of MoS2 resulting in quick transport of electrolyte ions to electrodes and rGO/ MoS_2 composites exhibited outstanding electrochemical performance with a specific capacitance 314.5 Fg^{-1}.

2.1.2. Solution Mixing

Solution mixing is widely used for preparing homogeneous graphene-based hybrid polymer composites with efficient interfacial bonding. In the processing of this technique, graphene and other desired fillers are dissolved in a solvent. Afterward, the polymer matrix is mixed to obtain a homogeneous solution. Moreover, magnetic stirring, fillers selection, ultrasonication, solvent adaptability, and mechanical agitation enable appropriate blending and distribution of components [20]. Solution blending is advantageous for obtaining a better filler distribution than mechanical mixing. The presence of a solvent highly facilitates the interfacial adhesion and control over the interaction, with a higher possibility of fabricating different functional additives between the filler and matrix to get a customized composite. However, this method has certain limitations, such as difficulties in achieving the stable and uniform dispersion of graphene sheets in the solvent, solvent compatibility with fillers, and solvent removal through final composite material by evaporation, oven drying, or freeze-drying [21]. Many references report graphene polymer composites using the solution method [22–24]. Barshutina et al. [25] reported graphene/CNT/ polydimethylsiloxane (PDMS) hybrid composite via water solution mixing and later calendaring in a three-roll-mill. In processing, CNTs and graphene (G) were homogeneously dispersed in separate solvents, and then both solutions were mixed, stirred, and ultrasonicated for 20 minutes and dried in a vacuum oven at 110 °C. Later, the dried CNT/G hybrid filler foam was soaked by PDMS and passed through a roll mill. The schematic process of preparation is shown in Figure 2. It was analyzed that G/CNT/PDMS composites offered excellent synergistic effects at ratio G/CNT (8:2) and exhibited outstanding electrical and mechanical properties.
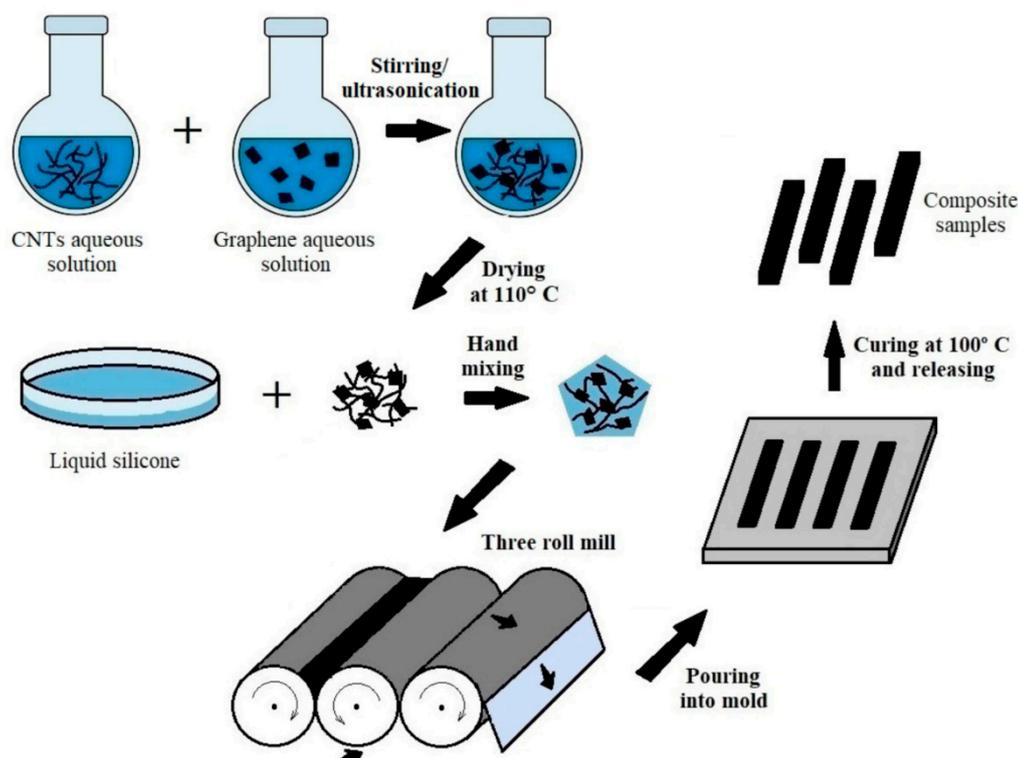
Figure 2. Schematic procedure for preparing G/CNT/PDMS hybrid composite by solution mixing approach. Reprinted with permission from Ref. [25].

2.2. Recent Preparation Methods for Graphene and Hybrid Polymer Composites

2.2.1. In-situ Polymerization

This In-situ polymerization is an effective method to fabricate graphene-based hybrid polymer composites, such that graphene sheets are incorporated and polymerized through a polymer matrix. This method is helpful to get a homogeneous dispersion of graphene in the polymer matrix, and subsequently, the final composite material has improved mechanical, thermal, and electrical properties. A monomer, a graphene source, and a catalyst are passed through the polymerization process during processing. In the schematic steps, a uniform solution is produced by the monomer dispersion in a solvent, and catalysts are introduced. Later, the dispersed graphene sheets are added to the solution. Catalysts initiate the polymerization process, and polymer chains are developed by encapsulating the graphene sheets, resulting in a highly connected network structure with enhanced properties [21,26]. Noh et al. [30] developed an excellently dispersed graphene/polymer composite with enhanced electrical conductivity by in situ polymerization of cyclic butylene terephthalate (CBT) oligomers. Before processing, the materials were moisture-freed by heating overnight at 110 °C then CBT and graphene powders were homogeneously mixed at 2000 rpm for 3 minutes by a high-speed Thinky mixer, and finally, the powder was used to prepare GNP-pCBT, GO-pCBT, and CCG-P-pCBT composites by heat pressing. Figure 3 shows a detailed illustration of the preparation steps. Many studies highlighted the significance of in-situ polymerization in fabricating graphene polymer composites [27–29].
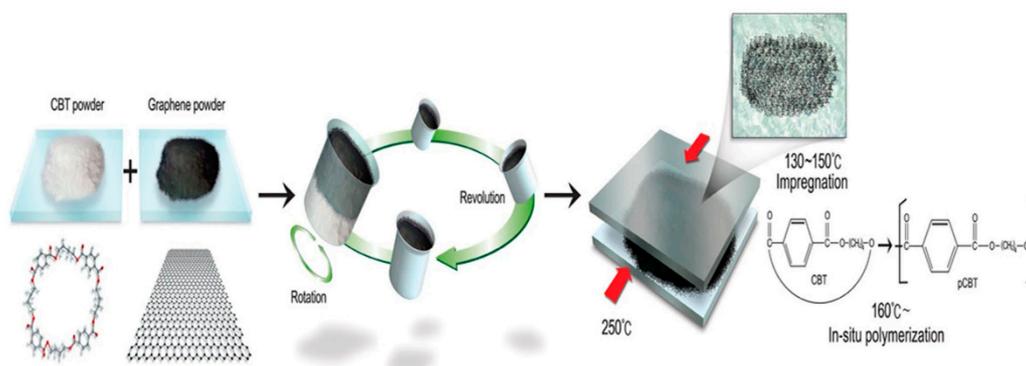
Figure 3. Schematic preparation of graphene/polymer composites by in-situ polymerization. Reprinted with permission from Ref. [30].

2.2.2. Electrospinning

Electrospinning is an outstanding approach to developing graphene-based hybrid polymer composites with desired aspect ratios and improved filler dispersion. During the procedure, [31] a uniform polymer solution is prepared using a compatible solvent, and graphene with other desired fillers is added to the polymer solution and homogenized by magnetic stirring and ultrasonication techniques. The electrospinning setup involves a high-voltage power source, a sharp-edge spinneret with polymer solution, and a grounded collector. The electric field is applied, and the charged polymer jet with intercalated nanofibers is deposited on the collector. Meanwhile, the solvent is evaporated, and the collected graphene-based hybrid polymer composite undergoes post-curing and thermal annealing. The resulting composite showed enhanced mechanical strength and higher thermal-electrical conductivity. This method offers higher control over composite thickness, filler dispersion, nanoscale structure, and fiber orientation, which makes it suitable for applications involving high surface-to-volume ratios [32–34].

Sarıipek et al. [35] successfully prepared the poly(ε-caprolactone) PCL-GO-Ag hybrid composite via electrospinning. Initially, a magnetically stirred solution containing Ag nanoparticles and graphene oxide (GO) was prepared, then added to the PCL solution and magnetically stirred to achieve a homogeneous solution. Later, the PCL-GO-Ag composite was obtained by electrospinning, as shown in Figure 4. The characterization results showed that the PCL-GO- 3.0% Ag composite achieved higher tensile strength, higher resistance to elastic deformation, and good antibacterial activity. Figure 4a Represents the surface modification of graphene to GO and treatment with AgNO3 to achieve GO-Ag layer, and Figure 4b depicts the magnetic stirring and electrospinning process.
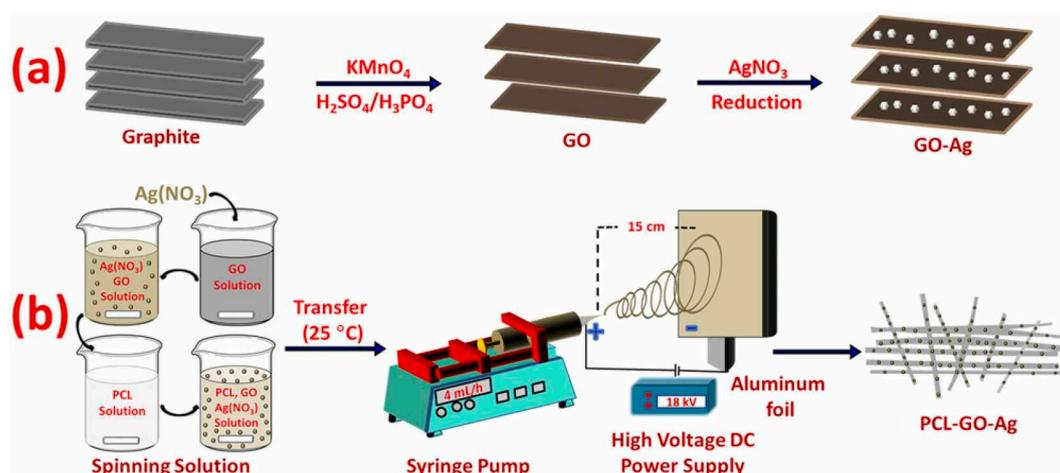
Figure 4. Schematic illustration of: **(a)** graphene surface modification processes; **(b)** solution mixing by magnetic stirring and later PCL-GO-Ag composite Fabrication by electrospinning approach. Reprinted with permission from Ref. [35].

2.2.3. Layer-by-Layer Assembly

Layer-by-layer (LBL) deposition is an ambient technique to fabricate graphene-based hybrid polymer composite films with highly controlled structures. The process involves depositing alternating layers of oppositely charged polymers and graphene materials on a template. The LBL method is carried out through the adsorption of a charged polymer onto the surface of an oppositely charged substrate. Later, the substrate is dipped into a polymer or graphene solution, allowing electrostatic interactions through charged species to lead to the adsorption process. After the first layer deposition, the extra material is washed out, and the procedure continues with the alternating material until the required number of layers is reached [36,37].

Wang et al. [38] adopted the LBL approach and developed polyethyleneimine (PEI)/ carboxylic acrylonitrile butadiene rubber (XNBR)/PEI/GO hybrid composite with negatively charged XNBR and GO was positively charged due to amino groups from PEI molecules as shown in Figure 5. The performed analysis revealed highly ordered GO and XNBR sheets with enhanced mechanical and electrical properties. Figure 5a shows the assembly process of XNBR latex, PEI, and GO sheets, and Figure 5b represents the final construction of the composite on a glass slide or silicon substrate.
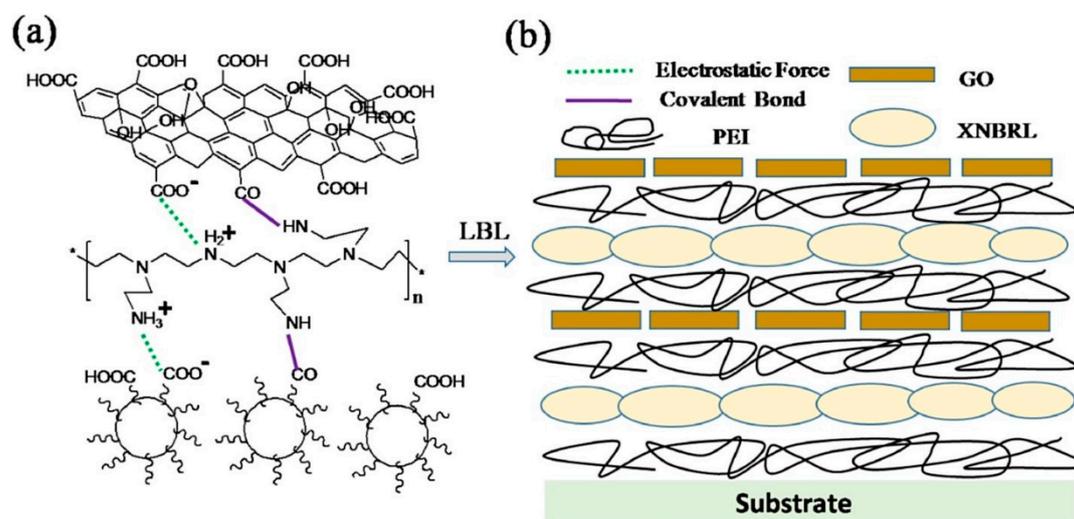

Figure 5. Schematic representation: **(a)** to develop PEI/XNBR/PEI/GO hybrid composite; **(b)** final composite design using LBL approach. Reprinted with permission from Ref. [38].

2.2.4. Chemical modification

Chemical modification is an advanced approach to synthesizing graphene-based hybrid polymer composites with heavily modified properties. This method chemically functionalizes graphene sheets with desired functional groups by covalent or non-covalent interaction. It offers high compatibility with polymer matrix and promotes strong interfacial interactions with better dispersion, resulting in improved mechanical, thermal, and electrical properties. The process involves different functionalization methods containing covalent functionalization. Herein, molecules are directly introduced onto the surface of graphene, and non-covalent functionalization involves non-bonding interactions to combine functional groups [1]. Covalent functionalization ways are usually followed by reactive functional groups, like epoxides or amines, to bond with the graphene surface.

Non-covalent functionalization involves various interactions to attach molecules on the graphene surface, such as π-π stacking, hydrogen bonding, or electrostatic forces. Finally, the chemically surface-modified graphene is introduced in the polymer matrix by solution blending, melt

mixing, or in-situ polymerization. As a result, a well-dispersed composite with high mechanical strength and thermal and electrical properties is obtained [39,40].

Jakubczak et al. [41] reported RGO/Al_2O_3-Ag nanocomposite with surface modification of metal oxide nanoparticles (M_xO_y) onto graphene family nanomaterials (GFMs) for filtration of drinking water. Figure 6 illustrates the chemical modification of graphene materials for water filtration properties.
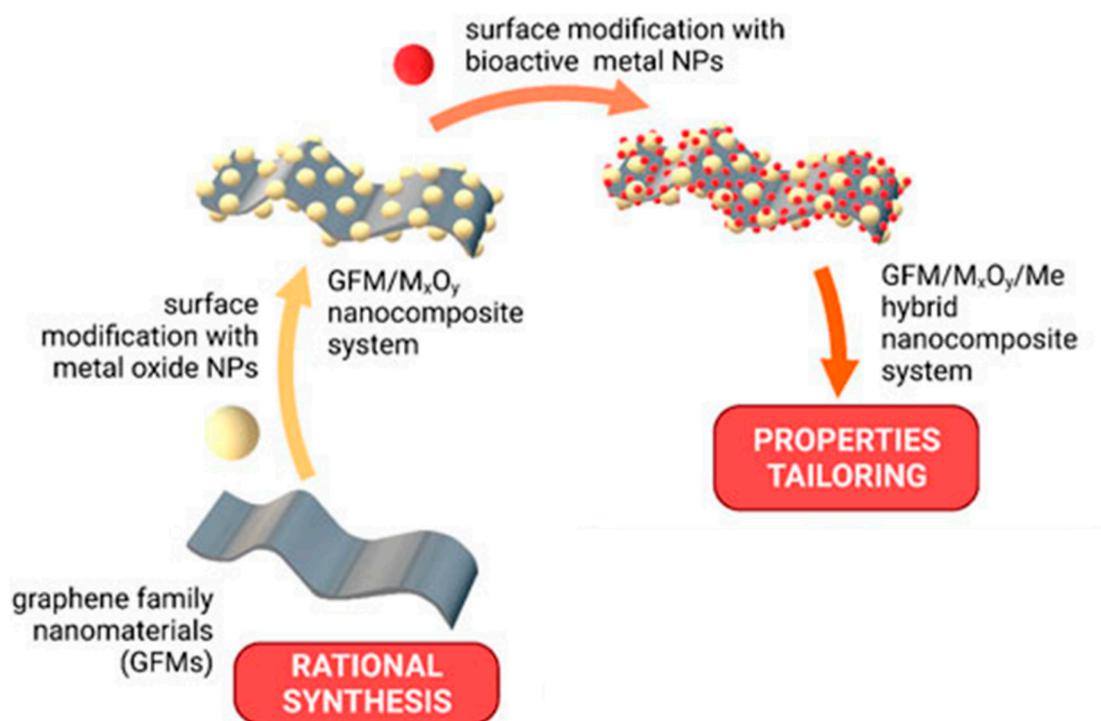

Figure 6. Schematic process of chemical modification of graphene nanomaterials for tailored bioactive properties. Reprinted with permission from Ref. [41].

3. Graphene-Based Hybrid Polymer Composites

Graphene-based hybrid polymer composites offer a groundbreaking performance due to the exceptional inherent properties of graphene and its synergistic relation with other fillers within a polymer matrix. This attitude synergistically favors tailoring properties such as mechanical strength, thermal conductivity, and electrical stability. The feasibility of controlling the arrangement and overall structure with minor surface modifications and functionalization has opened avenues for desired material design to tackle specific application requirements, revolutionizing industries from aerospace to electronics and developing the traditional fabrication processes. Wei et al. [42] summarized different processing techniques to produce functional polymer composites and demonstrated that fabrication methods significantly affect the performance, structure, and properties of polymer composites. Figure 7A shows a connected network structured GO/MWCNT /epoxy composite, Figure 7B depicts the combination of filler particles localized on corners of the polymer matrix, Figure 7C shows the connected morphology of olefin block copolymer/carbon black/thermoplastic polyurethane (OBC/CB/TPU) ternary mixture composites and Figure 7D demonstrates different filler surface modification strategies.
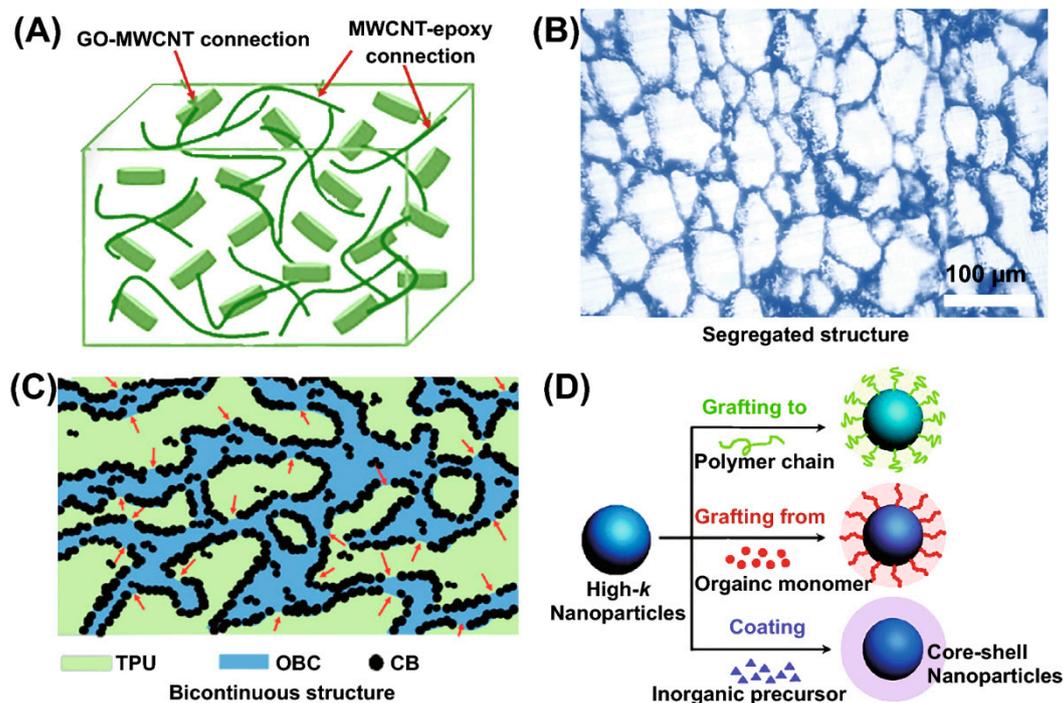
Figure 7. (A) Network structure of GO-MWCNT /epoxy composite; **(B)** Formation of segregated system by localized filler particles at the boundaries between the polymer grains; **(C)** Graphical interpretation of network structure of olefin block copolymer/carbon black/thermoplastic polyurethane (OBC/CB/TPU) ternary mixture composites; **(D)** Typical procedures associated with filler surface modification. Adopted with consent from Ref. [42].

Luo et al. [7] formed a 3-Dimensional (3-D) hybrid structure at various aspect ratios to achieve a synergistic effect with enhanced conductivity by introducing pristine carbon nanotubes (p-CNTs) and functionalized carbon nanotubes (f-CNTs) into conductive poly (methyl methacrylate)/graphene nanoplatelet (PMMA/GNP) composites. The composites were investigated for in-plane and through-plane electrical properties, and tunable conductivity anisotropy ranging from 0.01 to 1000 was achieved. Moreover, it was observed that, in the in-plane direction, the synergies of hybrid fillers are highly dependent on total filler content. Meanwhile, the GNP/CNT or GNP/f-CNT ratio was a key parameter in the through-plane path. Figure 8a–f shows the evolution of a micro-structural conductive network with the volume ratio of GNPs/f-CNTs.
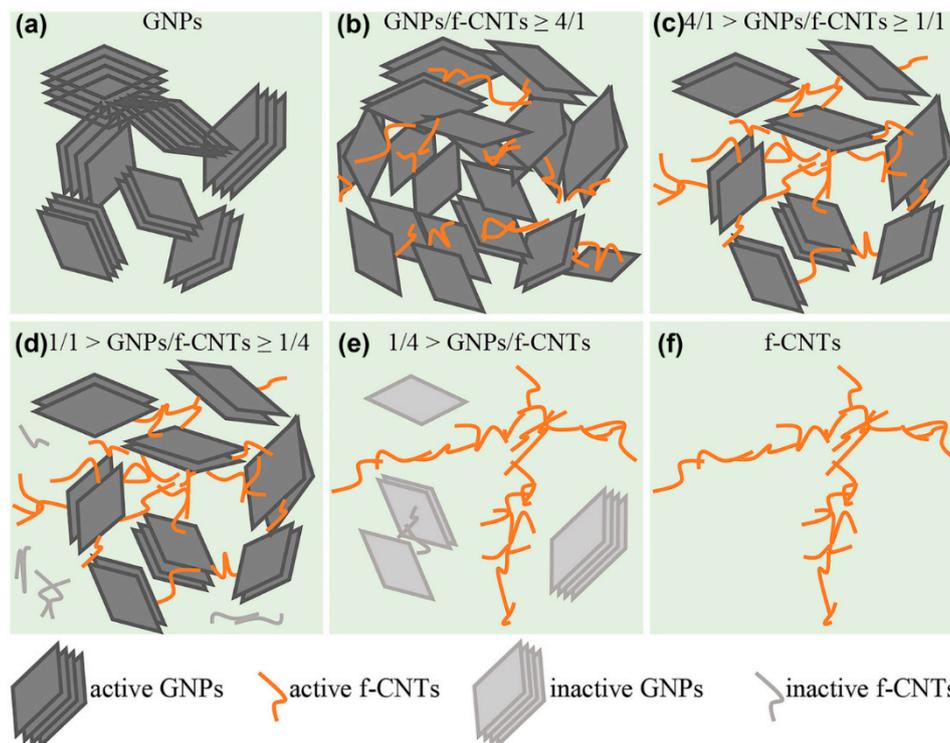
Figure 8. Schematic representation of conductive 3D network structure of PMMA/GNP/f-CNT composites as a function of decreasing content of GNPs/f-CNTs to interpret different synergistic behaviors. Conductive polymer composites containing: **(a)** single GNPs; **(b)** GNPs/f-CNTs ≥ 4/1; **(c)** 4/1 > GNPs/f-CNTs ≥ 1/1; **(d)** 1/1 > GNPs/f-CNTs ≥ 1/4; **(e)** 1/4 > GNPs/f-CNTs; and **(f)** single f-CNTs. Reprinted with permission from Ref. [7].

Huang et al. [43] designed GNP, MWCNT, and highly loaded epoxy composites and achieved a synergistically enhanced thermal conductivity with 10–50 vol% nanocarbon filler, e.g., (the composite with 20 vol% CNTs and 20 vol% GNPs shows a thermal conductivity up to 6.31 $Wm^{-1} K^{-1}$). Figure 9 Represents **(A)** the thermal conductivity comparison for individual CNTs, GNPs, and hybrid CNT+GNP filler at 40 vol% and **(B)** shows the morphology of the fractured surface of epoxy composites with individual CNT, GNP, and hybrid CNT+GNP fillers at 20 vol% to 40 vol%.
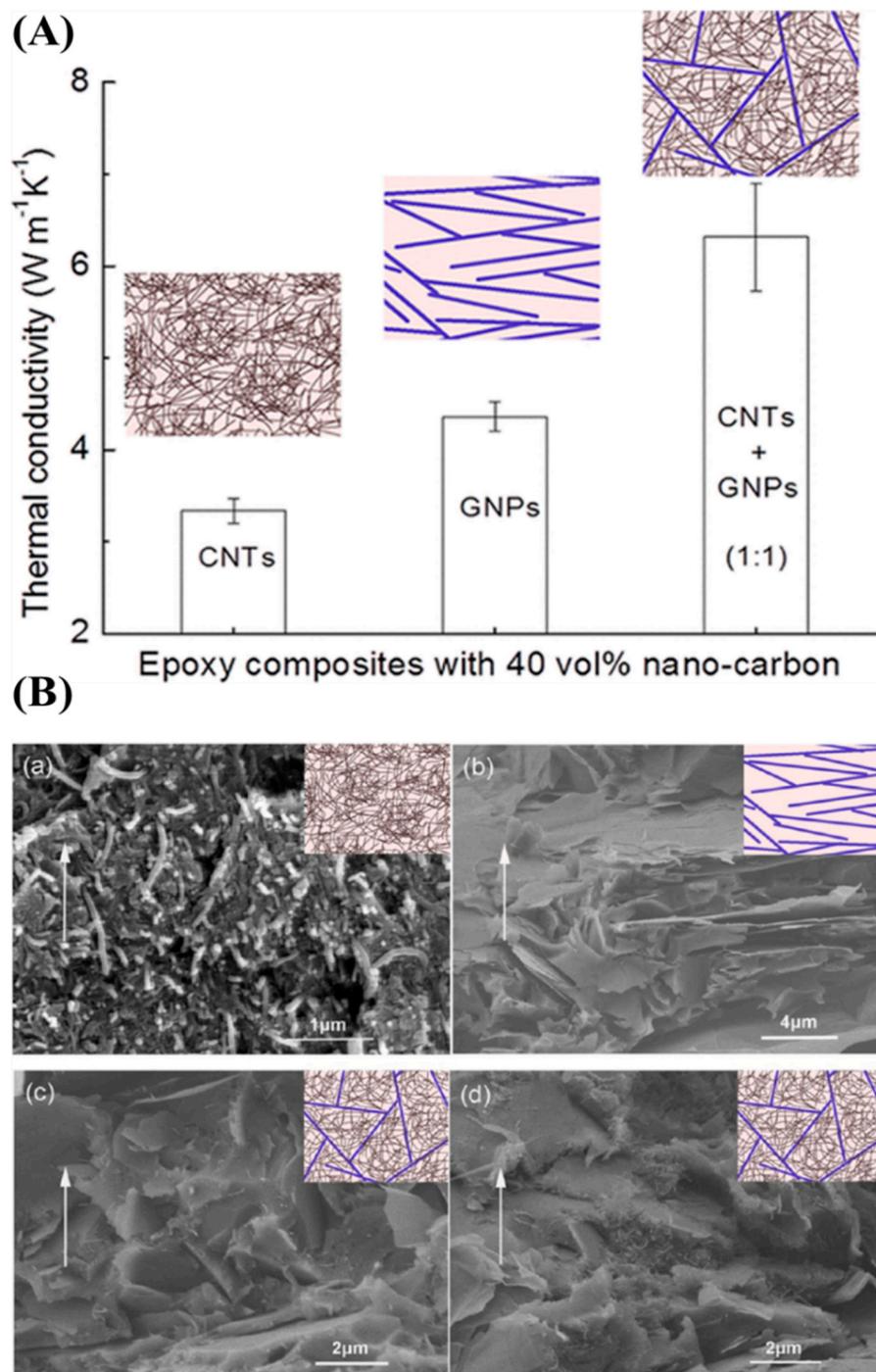
Figure 9. (A) Comparison of thermal conductivity of CNTs/GNPs epoxy composite to individual CNTs and GNPs at 40 vol%; **(B)** SEM images showing the morphology of fracture surface of the epoxy composites: **(a)** epoxy/CNT50, **(b)** epoxy/GNP50, and **(c,d)** epoxy/CNT25/GNP25. The arrows indicate the through-thickness direction of the composite samples, while the insets in the figures exhibit the nanocarbon dispersion in the composites. Reproduced and reprinted with permission from Ref. [43].

Yang et al. [44] designed epoxy composites with multi-graphene platelets (MGPs) and multi-walled carbon nanotubes (MWCNTs) and achieved improved mechanical properties and thermal conductivity due to synergetic effect. MWCNTs bridge adjacent MGPs and offer a high contact area between the MGP/MWCNT structures. Scanning electron microscope images showed that MWCNT/MGP hybrid nanofillers presented higher solubility and better compatibility than individual MWCNTs and MGPs, and the tensile strength of GD400-MWCNT/MGP/epoxy

composites was 35.4% higher than that of pure epoxy and thermal conductivity increased by 146.9% using GD400-MWCNT/MGP hybrid fillers. Figure 10 Demonstrates the preparation process of epoxy composites with different nanofillers.
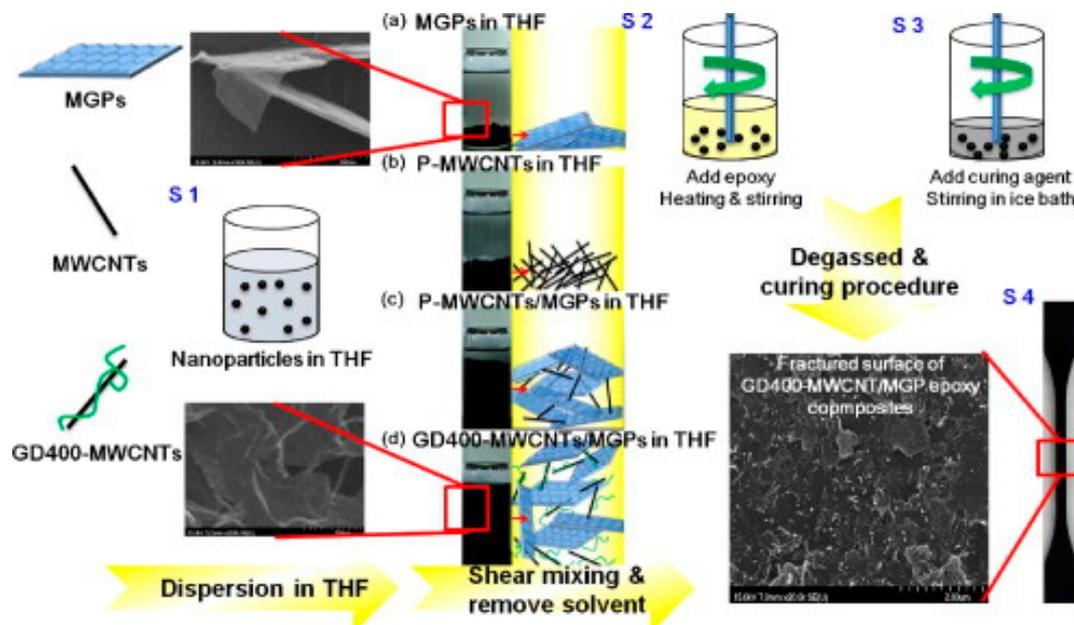

Figure 10. Preparation of epoxy composites with different nanofillers: **(a)** MGPs; **(b)** P-MWCNTs; **(c)** P-MWCNTs/MGPs; and **(d)** GD400-MWCNTs/MGPs, via solution mixing method. Reprinted with permission from Ref. [44].

4. Mechanical and Structural Properties

The presence of graphene and intercalated fillers through a polymer matrix offers a paradigm shift in material engineering due to its unique structural properties. Beyond other properties, graphene-based hybrid polymer composites possess remarkable tensile strength, high Young's modulus, significant resistance to deformation, improved toughness, and impact resistance, mitigating the propagation of cracks and fractures [45,46]. These composites can be customized to achieve specific mechanical properties by handling filler content, orientation, and interactions to fulfill the demands of the aerospace [47], electronics, automotive, and construction industries. Table 1. summarizes the increased mechanical properties (modulus, tensile strength) of graphene-based polymer composites prepared using different preparation methods reported in recently published research.

Table 1. Enhanced mechanical properties of graphene hybrid composites reported in currently published research papers.

Hybrid Filler	Hybrid Filler Content	Matrix	Preparation technique	Young's modulus and enhanced %	Tensile strength and enhanced %	Ref.
Multi-walled carbon nanotubes/multi-graphene platelets (MWCNTs/MGPs)	0.1/0.9 wt.%	Epoxy	Melt-blending	3350 MPa 22.6%	64.5 MPa 14.5%	**[44]**
GNP/Carbon black (CB)	2/24 wt.%	Ethylene–propylene–diene terpolymer rubber (EPDM)	Roll milling	20 MPa ≈198.5%	19.9 MPa ≈17.06%	[48]

Graphene foam/CF	0.5/10 wt.%	PDMS	Chemical vapor deposition (CVD)	3.05 MPa 185 %	2.50 MPa 63 %	[49]
GO/Short glass fibers (GF)	0.5/- wt.%	Polyether-sulphone (PES)	Extrusion compounding and Injection molding	7.3 GPa 25.4 %	119 MPa 10.2 %	[50]
GO/CFGO	0.1/1 wt.%	Polyurethane (PU)	Mechanical mix and Electrophoretic deposition	23.18 MPa -	62.04 MPa 46.4%	[51]
Reduced graphene oxide/ Silica (rGO/SiO$_2$)	1/99 30 phr (parts per hundred)	Styrene butadiene rubber (SBR)	Electrostatic assembly/ Roll mill	2.7 MPa 170%	17.34 MPa 1204%	[52]
GNP/GF	5/10 wt.%	PP	Melt mixing and injection molding	4.47 GPa -	45.4 MPa -	[53]
Short CFs /GO	12.5/0.5 wt.%	PES	Solution and melt mixing	7.79 GPa 31.7%	119.09 MPa 12.1%	[54]
3-aminopropyltriethoxysilane -functionalized graphene oxide (APTSi-GO)	1.5 wt.%	Polyimide (PI)	In situ polymerization and thermal imidization	- 132%	- 79%	[55]

5. Thermal Properties

The unusual thermal conductivity of graphene and collaborative structure with other fillers greatly facilitates efficient thermal conductive hybrid polymer production. Graphene interplay with various fillers offers synergistic effects within the polymer matrix and produces thermally conductive pathways that provoke heat transmission and thus enhance the composite's overall thermal conductivity [56,57]. Furthermore, the collaboration with fillers like nanoparticles, carbon fibers, and carbon nanotubes offers more efficient heat transfer mechanisms as each filler contributes to heat transmission. These highly thermally conductive composites are functional in electronics applications for advanced thermal management solutions, efficient energy storage, and conversion systems [58,59].

Table 2. Improved thermal conductivities of graphene hybrid polymer composites from published references.

Hybrid Filler	Hybrid Filler Content	Matrix	Preparation method	Thermal conductivity (Wm^{-1}K^{-1}) and %Increase @ pure matrix	Ref.
GNPs/MWCNT	20/20 vol%	Epoxy	Melt-blending	6.31 3055%	[43]
MWCNTs/MGPs	0.1/0.9 wt.%	Epoxy	Melt-blending	0.321 146.9%	[44]
GNP/CB	2/24 wt.%	EPDM	Roll milling	1.2 313.79%	[48]
GF/CF	0.5/10 wt.%	PDMS	CVD	0.55 162 %	[49]
GNP/GF	20/16 wt.%	PP	Melt mixing	5 times increase (pure PP)	[53]
APTSi-GO	1.5 wt.%	PI	In situ polymerization and thermal imidization	0.33 100%	[55]

GF + modified hexagonal boron nitride (M-h-BN)	33.8 wt.%	PDMS	CVD + Solution mixing	23.45 12928%	[56]
G/Cu nanoparticles	40/35 wt.%	Epoxy	Solution method	13.5 6650%	[60]
BN + reduced graphene oxide (rGO)	13.16 vol%	Epoxy	Ice-templated and infiltration	5.05 2425%	[61]
Expanded graphite (EG)/CNTs	20/1 wt.%	High density polyethylene (HDPE)	Melt blending	3.10 25%	[62]
EG/MWCNT	15/5 wt.%	PP	Melting method	1.52 442.86%	[63]
Al$_2$O$_3$/GNP	12 wt.%	Epoxy	Solution mixing	1.49 677%	[64]
Boron nitride nanosheets (BNNSs)/ Graphene	1.6/6.8 wt.%	Polyamide-6 (PA6)	Solution mixing	0.891 350%	[65]
Functionalized Graphene sheets with nanodiamond filler (FGS/NDs)	45 wt.%	Polyvinylidene fluoride (PVDF)	Solution method	0.66 257.14%	[66]

6. Electrical properties

Apart from other properties, graphene has remarkable electrical conductivity and integration in a polymer matrix with other fillers dramatically increases the electrical conductivity of the composite. Synergistic networks in graphene-based hybrid polymer composites enable consistent electron mobility and overall electrical conductivity of the composite [67,68]. The collaboration of graphene with carbon nanotubes, nanoparticles, and metallic nanoparticles further amplifies the electrical conductivity due to the individual contributions of each constituent. This transformative collaboration highly facilitates tailored properties, including conductive coatings, flexible electronics, and advanced sensors [26,69,70].

Table 3. Graphene hybrid polymer composites with enhanced electrical conductivities.

Hybrid Filler	Hybrid Filler Content	Matrix	Preparation method	Electrical conductivity	Ref.
APTSi-GO	1.5 wt.%	PI	in situ polymerization and thermal imidization	2.6×10^{-3} Sm^{-1}	[55]
EG/MWCNT	15/5 wt.%	PP	Melting method	159.62 Sm^{-1}	[63]
FGS/NDs	10 wt.%	PVDF	Solution method	7.1×10^{-7} Scm^{-1}	[66]
RGO sheets	10 wt.%	Amine-modified nano-fibrillated cellulose (A-NFC)	Solution casting	71.8 Sm^{-1}	[71]
Graphene	20 wt.%	Polypyrrole (PPy)	In-situ polymerization	7.930 Scm^{-1}	[72]
GNP/Short CF	0.02/0.08 vol%	Polymer	Theoretical modeling	10^3 Sm^{-1}	[73]
GNP	1.0 wt.%	Epoxy	3-roll mill	2.6×10^{-6} Sm^{-1}	[74]

7. Property Influencing Factors

7.1. Filler type and aspect ratio

Filler type and aspect ratio are the backbone of the fabrication of smart composites [75]. Graphene-based hybrid polymer composites hold great promise due to the discrete dimensions of graphene and other fillers. For instance, combining graphene with CNTs upholds micrometer lengths and 10-30 nm diameters. This scheme establishes a synergistically infiltrated network through polymers producing materials with superb electrical conductivity (1000-3000 Sm^{-1}), mechanical

strength, and thermal conductivity [76,77]. Furthermore, graphene combined with metal nanoparticles like gold (Au), silver (Ag), and copper (Cu) offers nanoscale dimensions (< 100 nm in diameter) and produces a highly connected network structure in the polymer matrix, presenting a higher electrical conductivity of 10^7 Sm^{-1} [78,79]. Besides the dimension, filler loading influences the composite's mechanical and physical properties [80]. Long fibers, e.g., CNTs and CFs, can make a continuous network in a polymer matrix even with low loading, which precedes excellent stress distribution, heat dissipation, tensile strength, and resistance to structural deformation [79]. Conversely, the low aspect ratio of short nanoparticles results in gaps and irregular networks, which hinder the overall performance of the composite. Nevertheless, filler type, size, and aspect ratio are crucial to producing composite materials with tailored properties for specific applications [81].

7.2. Filler-matrix compatibility

Filler-matrix compatibility is a crucial factor in achieving robust and flawless composites. Graphene's 2D structure, nanometer size, and high surface area aid in the infusion capability to fabricate polymer composites with interlinked structures and expanded properties [43]. A well-maintained filler-matrix compatibility aids in realizing a uniform dispersion of filler and ordered structure with tailored properties [82–84]. Li et al. [85] developed dopamine (DA) modified graphene oxide (GO) and copper nanowires (Cu NWs) hybrid epoxy composites, and with the proportion of Cu-NWs @PDA: GO@PDA 7:3 an effective filler matrix compatibility was observed, which resulted in higher thermal conductivity of 0.36 Wm^{-1} K^{-1} with outstanding electrical insulation properties. Conversely, due to strong Van der Walls forces, high aspect ratios of graphene lead to agglomeration and non-uniform dispersion through polymer matrix [86]. Graphene is surface functionalized using different chemical groups or polymers to break the barrier, increasing the interfacial bonding and interaction between the filler and matrix. Romasanta et al. [87] successfully produced functionalized graphene sheet (FGS) filled poly(dimethyl)siloxane nanocomposites and, at 2 wt.% FGS, a high dielectric constant was realized with high mechanical properties.

7.3. Homogeneity of dispersion

In fabricating excellent hybrid polymer composites, homogeneous dispersion is a key factor in determining the performance and properties. In Graphene-based hybrid composites, [13] first graphene and other fillers are evenly dispersed and later uniformly distributed in a polymer matrix. Good dispersion results in symmetrical structure and significantly boosts mechanical properties, i.e., fracture resistance, high tensile strength [88], and load-bearing facilities. Electrical and thermal conductivities are also improved, facilitating continuous charge transport, sensors, and heat management applications [85]. Tuichai et al. [89] prepared well-dispersed Ag-rGO/ polyvinylidene fluoride (PVDF) composites by seed-mediated growing technique and achieved highly connected microstructure with high dielectric constant. However, lousy dispersion [90] results in agglomeration and uneven distribution within hybrid fillers and polymer matrix and severely demoralizes the composite capabilities. Such composite presents an irregular and non-uniform structure, leading to mechanical disruptions and ineffective electrical and thermal conductivities due to interrupted pathways [91].

7.4. Processing techniques

Composite processing methods are pillars to achieve uniformly distributed microstructure with expanded properties. The fabrication techniques involving compression mold, 3D printing, and filament winding affect the filler placement inside the matrix. Fabrication of graphene-based hybrid polymer composites with uniform distribution of graphene highly aids in fully harnessing graphene's unique properties and synergistic relation with other fillers [14,92]. However, the tendency of graphene layers to attach precedes clustering issues. Thus, efficient processing strategies, e.g., sonication, high shear mixing, and extrusion methods, aid homogeneous graphene dispersion and increase its reinforcing effect on the composite [93,94]. Moreover, curing conditions, e.g., time or

temperature, significantly impact the interfacial bonding and load transfer ability between filler and matrix, improving the composite's mechanical properties and durability. Additionally, specific processing methods, e.g., 3D printing, electrospinning, spray coating, or shear-induced alignment, provide better control over the graphene orientation to get complex geometries with tailored anisotropic properties and the choice of preparation process dramatically impacts the cost-effectiveness and scalability of composites [95,96].

7.5. Post-treatment and functionalization

Post-treatment processes such as surface treatments and protective coatings of composites significantly increase their resistance to humidity and corrosion. Graphene filler and polymer matrix interaction are highly sensitive to environmental conditions, and surface treatments can significantly improve the composite resilience [97–99].

On the other hand, functionalization can be tailored to exploit the unique properties of graphene. By modifying the graphene surface with specific functional groups or incorporating other nanoparticles, functionalization can enhance electrical and thermal conductivity or even provide additional functionalities like sensing capabilities. This level of customization is particularly advantageous in applications where precise control over material properties is required, such as in advanced electronics or sensors [100,101]. Functionalization opens new possibilities for graphene-based composites, enabling them to excel in areas where traditional materials fall short. In essence, post-treatment and functionalization strategies in graphene-based hybrid filler-polymer composites constitute sophisticated techniques that unlock the full potential of these materials. They ensure the composite's robustness and longevity and empower it with diverse functionalities [102,103]. As the field of materials science continues to evolve, the synergy between graphene and tailored post-treatment and functionalization processes offers exciting prospects for developing innovative and high-performance materials that can revolutionize various industries [104].

8. Applications

8.1. Aerospace Evolution: Lightweight Structural Components for Enhanced Performance

Graphene-based hybrid polymer composites are excellent candidates for aerospace applications due to exceptional mechanical properties, e.g., strength, stiffness, and lightweight, to create robust structural components. The combination of lightweight, higher Young's modulus and tensile strength improves fuel efficiency, payload capacity, and overall aircraft efficiency [105]. Moreover, these composites can resist extreme temperature conditions, mechanical stress, and corrosion, making them suitable for aircraft frames, wings, and engine components. Space shuttles and high-velocity aircraft need a thermal management system to dodge overheating and structural issues. Graphene composites serve in thermal protection systems, heat shields, and thermal barriers due to their excellent thermal conductivity [69,106]. Figure 11 shows potential applications of graphene-based polymer composites in different aspects of aerospace industries.
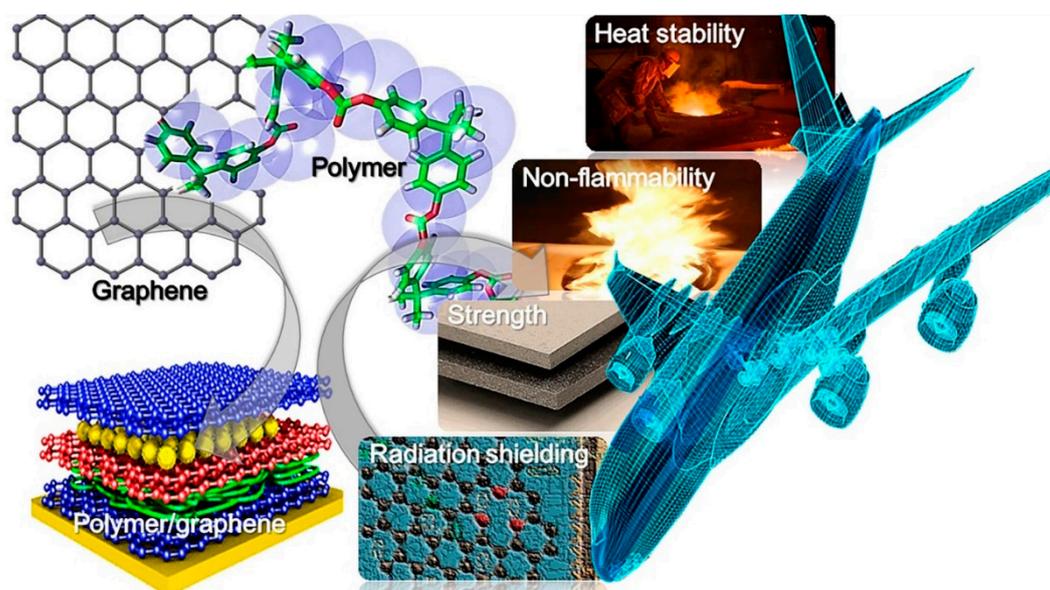
Figure 11. Multiple roles of graphene hybrid polymer composites in aerospace applications. Reprinted with permission from Ref. [107].

Furthermore, installing graphene composite-based sensors in aircraft provides real-time surveillance of structural deformation. Lightning strikes during flights cause severe accidents due to the absence of electrically conductive materials in manufactured parts, while graphene-based hybrid composites have excellent thermal and electrical conductivity and are favorable to resolving lightning strike problems [108]. Furthermore, space exploration demands robust materials to tolerate extensive radiation and vacuum conditions [109]. Graphene-based hybrid composites offer impressive radiation shielding, mechanical strength, and thermal stability to manufacture spacecraft components orientated for unforgiving space environments. However, utilizing the full potential of these composites encounters issues like cost-effectiveness, regulatory compliance, scalability, and standardized practices [110,111].

8.2. Advanced Electronics: High-Performance Conductive Materials and Flexible Circuits

Lightweight graphene-based hybrid polymer composites [113] exhibit high-performance conductive coatings, optimal fuel efficiency, efficient heat dissipation [114], effective signal transmission, and electromagnetic shielding in electronics, given their significant electrical and thermal conductivity [112]. These composites are perfect for flexible circuits and wearable devices due to their flexibility and lightweight nature [115]. Moreover, the synergy of their electrical and thermal properties with mechanical ability has revolutionized smart textiles, sensors [116], and integrated electronic systems [117,118]. Li et al. [119] presented an orientated assembly of giant graphene oxide (GGO) sheets via 3D printing and achieved flexible patterns with high surface area and enhanced electrical conductivity of up to 4.51 ($\pm$ 0.18) $\times 10^4$ Sm^{-1}. Moreover, these orientated patterns were tested for the electrically driven soft actuators, offering controlled deformation at lower voltage. Figure 12 shows a detailed analysis and fabrication process of graphene hybrid composites in flexible and printable electronics by manufacturing a soft actuator with printed RGO electrodes. Figure 12a illustrates the electrical stimulation of the bilayer RGO/PDMS actuator. Figure 12b shows the maximum bending angle as a function of driving voltage, Figure 12c the digital images of the reversible shape change of the actuator at different bending angles, and Figure 12d the hand-shaped actuator with independent control of the fingers by various gestures.
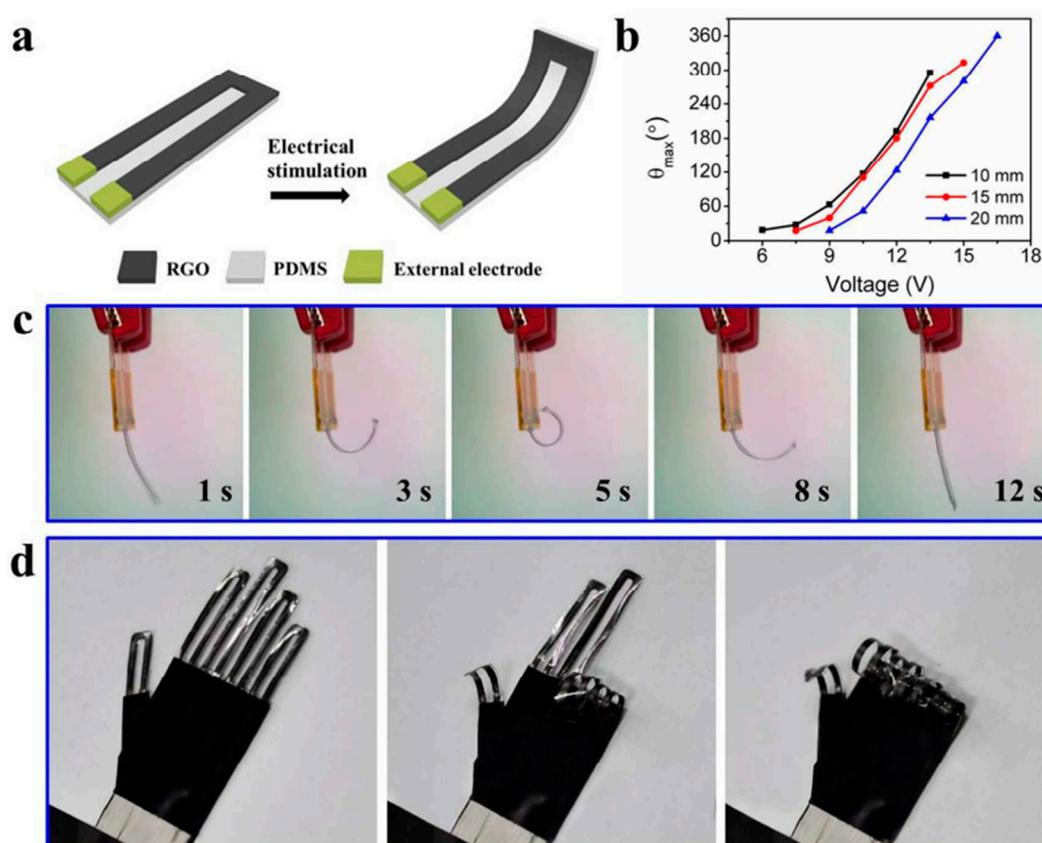
Figure 12. Manufacture of the soft actuator with printed RGO electrodes: **(a)** RGO/PDMS bilayer actuator under electrical stimulation; **(b)** Maximum bending angle of the actuators as a function of driving voltage; **(c)** Digital images of the actuator at various bending angles, with reversible shape change of the actuator; **(d)** Final look of Hand-shaped actuator with independent control of the fingers by various gestures. Reprinted with permission from Ref. [119].

8.3. Energy Storage Revolution: Efficient Batteries and Supercapacitor

Graphene-based hybrid polymer composites have revolutionized energy storage technologies [120]. The remarkable electrical conductivity and large surface area lead to elevated energy storage in batteries and supercapacitors by facilitating faster charging and discharging rates, extending battery lifetime, and improving energy density. This progression addresses the energy demands of portable electronics, renewable energy storage systems, and electric vehicles, resulting in green energy solutions [121,122]. These composites' electrical and thermal properties also offer competent solar cells and thermoelectric generators by improving electron mobility, light absorption, and thermal conversion, resulting in efficient waste heat recovery [115]. He et al. [123] fabricated a skinny (0.5 mm width) graphene-based paper-like electrode for a micro-supercapacitor with a current density of 0.5 to 5 A.cm^{-3} and exhibiting high volumetric capacitance of ~3.6 F·cm^{-3} with highly high specific capacitance retention of up to 94% even after 20000 cycles. Figure 13 shows the detailed preparation process of composite and integration in micro-supercapacitor.
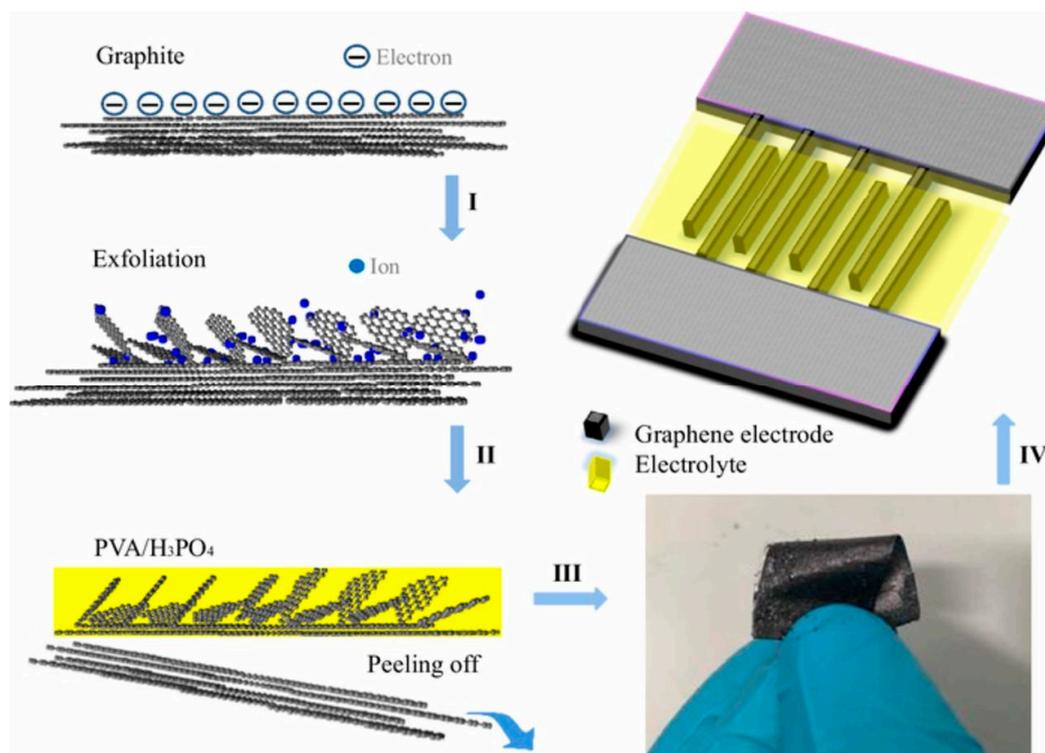
Figure 13. Preparation process of micro-supercapacitor: **(I)** electrochemical exfoliation of graphite foil; **(II)** coating the graphene/graphite foil with gel electrolyte (PVA/H3PO4); **(III)** Peeling off flexible graphene paper-like electrode; **(IV)** building of the interdigitated micro-supercapacitor devices using the electrode paper. Reprinted with permission from Ref. [123].

8.4. Transportation Innovation: Lightweight Automotive Components for Enhanced Efficiency

Graphene-based hybrid polymer composites are fundamental in developing robust and fuel-efficient vehicles due to their unique mechanical and lightweight properties. The high electrical conductivity of graphene-based composites dramatically improves the charging efficiency of lithium-ion batteries, resulting in optimum battery lifetimes in electric vehicles [124]. High mechanical strength [6] and higher flexibility facilitate tailored, impact-resistant, and safely enhanced vehicle modules [125]. Furthermore, outstanding thermal conductivity influences electric vehicles' energy efficiency and component durability by heat dissipation through batteries, electric motors, and power electronics [126–128]. Figure 14 presents various graphene composites examined for load-bearing and structural automotive applications, such as seats for Daimler Chrysler sports cars, a diagonal support beam for Porsche, and bumper structures for BMW.
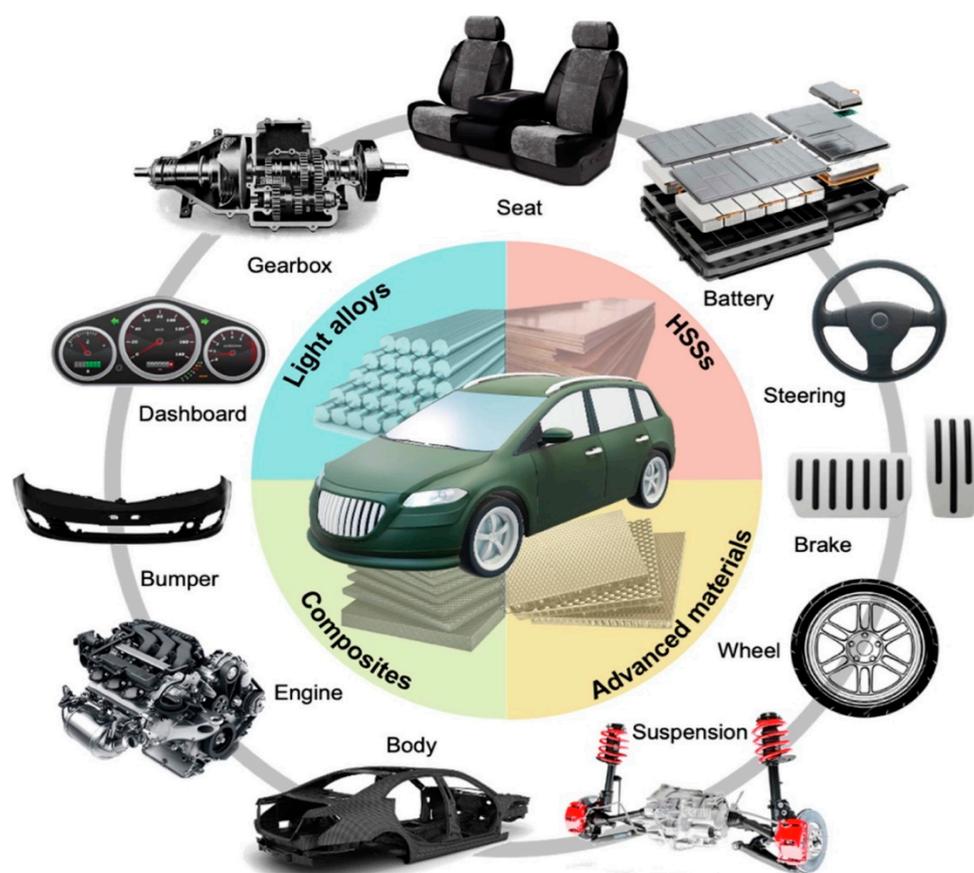
Figure 14. Role of graphene and advanced hybrid polymer composites in load-bearing automobile structure preparation [129]. Reprinted with permission from Ref. [130].

9. Conclusion

This literature review summarizes the panorama of graphene-based hybrid filler polymer composites involving conventional and advanced preparation techniques, a detailed analysis of graphene-based hybrid polymer composites related to enhanced mechanical, thermal, and electrical properties reported in different research papers, the influencing factors to attain well-organized composite structures with improved properties and critical applications in diverse fields and heavy industries. It was concluded that traditional preparation techniques are simple and easy to work with but show deficits like homogeneity, surface integrity, and balanced dispersion of fillers through the polymer matrices. However, modern fabrication techniques, e.g., surface functionalization, electrospinning, and additive manufacturing, offer a controlled homogeneous dispersion to form connected structures and highly facilitate the synthesis of graphene hybrid fillers and introduction to polymers. The synergistic effects of graphene are widely explored, as many studies reported that incorporating graphene hybrid fillers in polymers drastically enhanced the mechanical strength, Young's modulus, and bending strength. Moreover, the thermal ability and electron mobility were highly expanded. The factors affecting the properties of graphene-based hybrid polymer composites, such as filler loadings, filler type, graphene orientation, filler-matrix compatibility, homogeneous dispersion, and post-treatments, are discussed in detail. Furthermore, these composites were explored for critical applications across aerospace, automotive, electronics, and energy storage devices.

10. Future Perspectives

Although many practical and theoretical studies have been proposed, several challenges exist to attain the expected results. Firstly, there is still a higher possibility of strengthening the interfacial

contacts by surface engineering graphene with other fillers and polymer matrices to utilize the synergistic interactions, resulting in extraordinary composite properties. Secondly, along with superior properties, large-scale production relies on manufacturing costs. Thus, one should consider the critical role of cost-effectiveness and scalability in widespread industrial applications while fabricating composites. Lastly, a few studies address these composites' harmfulness and environmental effects; thus, as a commercial product, huge attention and exploration is needed for monitoring and safety concerns of these composites to ensure their responsible use in different applications.

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