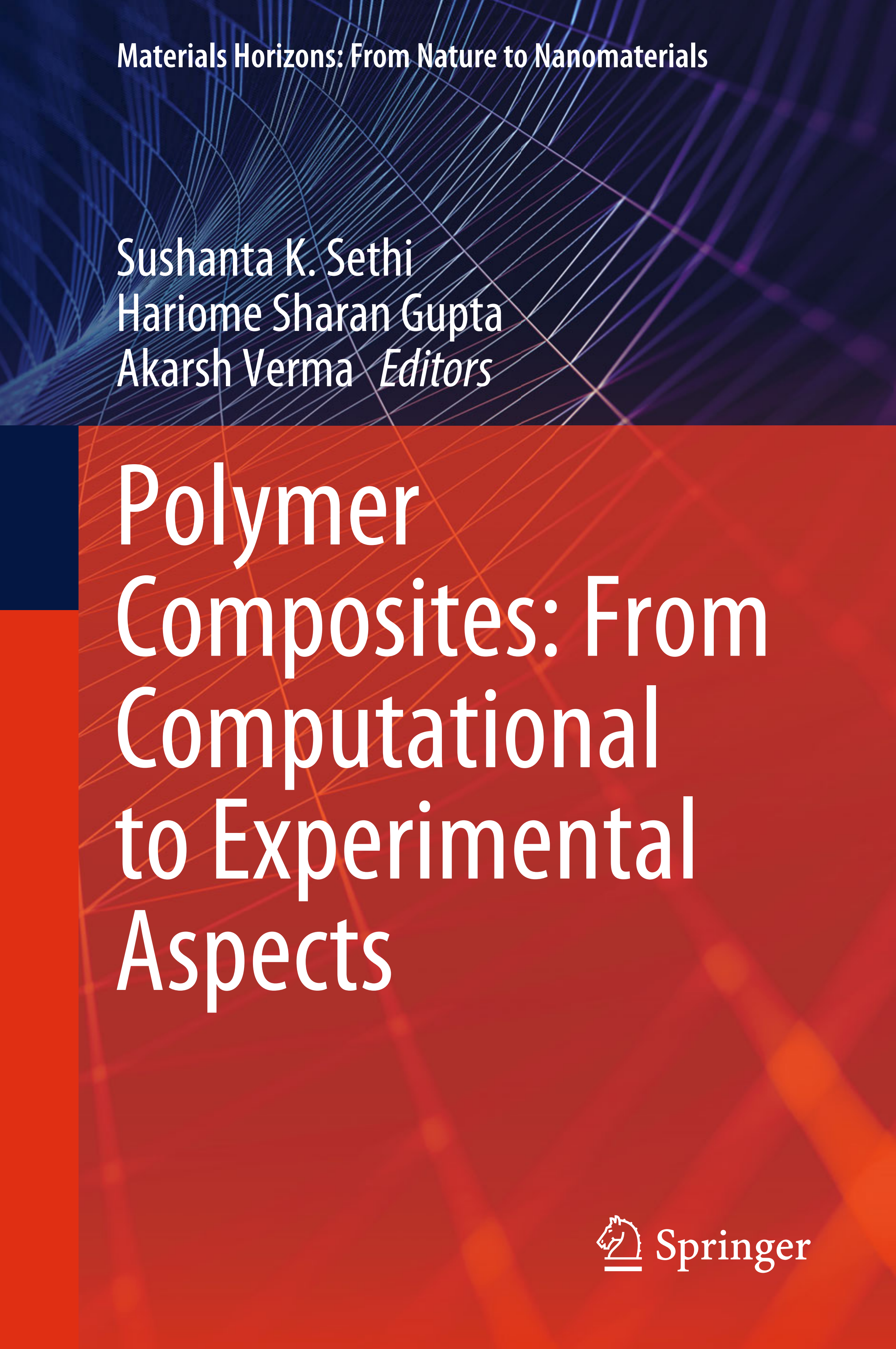

Materials Horizons: From Nature to Nanomaterials

Sushanta K. Sethi
Hariome Sharan Gupta
Akarsh Verma *Editors*

Polymer Composites: From Computational to Experimental Aspects

Springer

Materials Horizons: From Nature to Nanomaterials

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Polymer Composites: From Computational to Experimental Aspects

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Chapter 1
Polymer Composites: Synthesis, Application, and Basic Theoretical Aspects

Nishtha Arora, Sachin Dua, Smruti Vardhan Purohit, Bibek Dash, Manishkumar D. Yadav, Bikash Kumar Jena, and T. Senthilkumar

Abbreviations

Sr. No.	Abbreviations
(1) Polymer matrix composite	PMC
(2) Polystyrene	PS
(3) Fiber-reinforced polymer	FRP
(4) Polycarbonate	PC
(5) Polyethylene	PE
(6) Polypropylene	PP

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(7) Polyether Ether Ketone	PEEK
(8) Polybenzimidazole	PBI
(9) Poly(vinylalcohol-leucine)	PVAL
(10) Poly(lactic acid)	PLA
(11) Polycaprolactone	PCL
(12) Multi-walled carbon nanotube	MWCNT
(13) Carbon nanotube	CNT
(14) Single-walled carbon nanotube	SWCNT
(15) Electromagnetic interference	EMI

1 Introduction to Polymeric Composites

1.1 Definition and Overview

Polymers have been fundamental in advanced applications for an extended period due to their versatility and ease of molding to specific needs [1]. Nonetheless, using a single polymer often falls short of meeting the demands of advanced applications. Consequently, polymer composites have gained worldwide attention. A composite material consists of two or more distinct phases—a matrix/continuous phase and a dispersed phase—resulting in bulk properties vastly different from any individual constituent. The matrix phase, primarily continuous, plays a pivotal role by hosting and sharing the load with the dispersed (reinforcing) phase. The reinforcing phase, typically more robust than the matrix, is embedded in a discontinuous form within the matrix. This reinforcing phase contributes significantly to the composite's overall strength, earning it the designation of a reinforcing phase [2]. These composites can incorporate metals, carbon, ceramics, and other polymers as matrices and reinforcements [1]. The exceptional chemical resistance offered by polymers rivals that of metals. Additionally, key properties like mechanical strength, corrosion, and fatigue resistance are notably higher in polymer matrix composites (PMCs) than in metals. The incorporation of reinforcing agents in polymer matrices leads to substantial enhancements in mechanical, electrical, and thermal characteristics. Incorporating polymers into the matrix can be achieved through diverse approaches, primarily involving methods like melt intercalation, solution blending, or in-situ polymerization. By blending fibers and polymers in various combinations, novel materials with outstanding performance characteristics can be tailored to meet diverse needs. Furthermore, in addition to fibers, various fillers, including $CaCO_3$, clay, mica, and glass microspheres, are repurposed to enhance the properties of polymers (Fig. 1) [1]. While the characteristics of the reinforcing elements greatly influence a composite's final properties, the initial material quality and chosen production methods also significantly affect its performance. The objective of composite manufacturing is to create components that exhibit desired traits by amalgamating the strengths of fibers

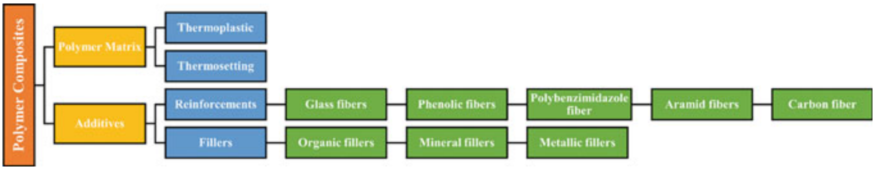

Fig. 1 Schematic representation of components of polymer composites

or particles with the matrix while simultaneously reducing or concealing their individual shortcomings [3]. PMCs can be crafted through various fabrication methods, each influencing the mechanical and physical traits of the final product. The properties of these composites rely on factors like the reinforcement type, volume ratio, how layers are stacked, their orientation, and the total number of layers. The choice of manufacturing techniques is predominantly guided by the type of polymer, be it thermoplastic or thermosetting, owing to their distinct chemical and physical characteristics [4]. When polymer-based composites are combined, they exhibit outstanding qualities such as essential thermal expansion properties, cost-effectiveness, convenient manufacturing, resistance to corrosion and abrasion, fatigue resistance, exceptional specific strength, stiffness, and lightweight nature. PMCs hold immense significance across diverse sectors, including electronics, industry, construction, marine, civil engineering, household, energy, military, sports, communications, medicine, aerospace, and automotive industries due to their exceptional attributes [5]. The chapter extensively explores various facets of synthesizing polymer composites, covering techniques like melt intercalation, solution mixing, and in-situ polymerization while incorporating a wide array of fillers and reinforcements. Additionally, the chapter delves into the detailed significance of these composites across diverse sectors, including construction, healthcare, aerospace, automobiles, electronics, and marine applications.

1.2 Historical Development

The modern age of composite materials commenced with the advent of synthetic plastics, replacing traditional natural resins sourced from plants and animals that were formerly the sole binding agents. In the early 1900s, the development of plastics like vinyl, polystyrene (PS), phenolic, and polyester surpassed the capabilities of natural resins [6]. However, pure plastics lacked adequate strength for certain structural uses, necessitating reinforcement for enhanced strength and stability. In a pivotal moment in 1935, Owens Corning unveiled fiberglass, a glass fiber that, when blended with plastic polymers, yielded an exceptionally robust and lightweight structure, marking the genesis of the fiber-reinforced polymers (FRPs) industry [7]. Following World War II, a burgeoning composites industry emerged as a niche, led by innovators like Brandt Goldsworthy, frequently hailed as the “grandfather of composites.” Goldsworthy spearheaded the creation of novel manufacturing techniques and products, notably the groundbreaking fiberglass surfboard that transformed the realm of sports. The 1970s witnessed a maturation phase within the composites sector, characterized by advancements in plastic resin technology and the enhancement of reinforcing fibers. DuPont’s development of Kevlar, an aramid fiber known for its exceptional tensile strength, high density, and lightweight properties, stood as a hallmark achievement. Concurrently, carbon fiber emerged during this era and progressively began replacing steel components. Presently, the composites industry remains dynamic, with a significant focus on renewable energy ventures. Notably, the manufacture of wind turbine blades is a leading area of growth, where advanced composite materials continually push the boundaries of size and efficiency. Goldsworthy’s pioneering contribution to composites included the invention of pultrusion, a manufacturing process pivotal for producing consistently robust fiberglass-reinforced products. In the contemporary landscape, this process finds extensive application across a diverse spectrum, encompassing tool handles, arrow shafts, ladder rails, railway flooring, pipes, protective covering, and healthcare instruments. In India, the introduction of advanced composites traces back to 1980 when Dr. APJ Abdul Kalam utilized them to craft the nozzle for the Satellite Launch Vehicle (SLV-3). Dr. Kalam stands as a pioneering figure in advancing research in this field and rightfully earns the title of the “father of advanced composites” within the country. PMCs represent a significant composite material category with a broad spectrum of applications. The growth of advanced composites in India can be attributed to the diverse array of raw materials available, various processing technologies, and their adaptability for shaping into intricate forms. However, achieving the optimal composite product in terms of cost-effectiveness hinges on identifying the perfect amalgamation of raw materials and processing techniques, all contingent on its processability [8, 9]. In the present day, composite materials are witnessing a rapid expansion of their usage across industries like automotive, appliances, and consumer goods. Additionally, composites are entering the realm of nanotechnology, showcasing a promising future in this domain. According to market data analysis, the composites market size reached USD 86.56 billion in 2021 and is anticipated to attain USD 150.28 billion by 2028, with an estimated Compound Annual Growth Rate (CAGR) of 8.2% between 2022 and 2028 (Fig. 2) [10].

1.3 Importance and Applications

In today’s technologically advanced society, polymers and their composites have emerged as pivotal materials for a wide array of practical applications. Owing to extensive research and expanding knowledge, polymer-based materials have taken the lead and are swiftly displacing other materials in various domains [11]. Constant advancements in polymer-derived materials provide viable alternatives to traditional substances, even in sectors where polymers were historically deemed unsuitable.

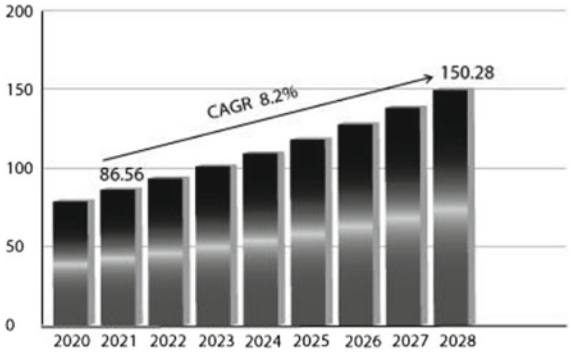

Fig. 2 Global composites market size by 2020 to 2028 (USD Billion). Adapted from ref. [10]

Notably, polymers have now stepped in as substitutes for metals and ceramics, particularly in industries such as construction, aerospace, automotive, and healthcare [12]. The trajectory is clear that this paradigm shift toward polymers will persist, propelled by their inherent characteristics and potential for sustainability [5]. When polymer-based composites are combined, they present exceptional qualities such as precise thermal expansion attributes, cost-effectiveness, effortless manufacturing, resilience to corrosion and abrasion, excellent fatigue resistance, high specific strength, elevated rigidity, and lightweight nature. The significance of PMCs reverberates across a multitude of sectors, including construction, household, energy, defense, industrial, sports, marine, communication, electronics, civil engineering, healthcare, aerospace, and automotive, due to their unparalleled attributes [5, 13].

1.4 Polymer Matrix Materials

Matrix material is a continuous phase that bonds the fibers together [14]. PMCs have garnered significant attention primarily because of their cost-effectiveness and superior specific strength and stiffness when compared to traditional metallic alloys. Furthermore, PMCs provide increased design versatility and enhanced resistance to both corrosion and fatigue [15].

The matrix materials employed in polymer composites play a pivotal role in influencing the composite's overall properties and performance. They contribute to both shape and size stability in the end product and enhance the material's ability to withstand outdoor conditions and maintain its stability. The selection of the matrix material depends upon the particular application and the intended properties sought for the composite. Matrix materials should be coordinately considered and selected from the three aspects of usage performance, processing property, and economic efficiency [14]. PMCs are composed of a polymer matrix, which can be either thermoplastic materials like polycarbonate (PC), polyvinylchloride, nylon, and PS, or thermoset materials such as unsaturated polyester and epoxy. These matrices are combined with a dispersed phase consisting of materials like carbon, ceramics, glass, and other polymers in the form of fibers or particles [16]. Traditionally, thermoset-matrix composites have been more prevalent, but there is currently a rapid evolution and development of thermoplastic-matrix composites [17].

1.4.1 Thermosetting Polymer Matrix

Thermosetting polymers retain their hard and non-softening characteristics when subjected to heat. They consist of a network of polymers with covalent bonds that resist movement at elevated temperatures. These thermosets are in high demand due to their three-dimensional cross-linked structure, which imparts exceptional attributes like temperature and solvent resistance [18]. Thermosetting polymer matrix materials offer a range of merits that make them suitable for diverse applications. This includes high-temperature resistance, excellent dimensional stability, chemical resistance, high strength and stiffness, low creep, excellent adhesion, electrical insulation properties, durable coatings, rigidity and hardness, excellent chemical stability, and more [8, 18]. While thermosetting polymer matrix materials offer many advantages, it's crucial to note that they also have limitations, such as the inability to be remelted and reshaped after curing. This irreversibility can be a drawback in some situations. The choice of matrix material should consider the specific requirements of the application to ensure the best performance. Thermosetting composites find a wide array of applications, ranging from aerospace structures like fuselages, airframes, nose cones, and re-entry surfaces to automotive, railway, and wind turbine components. They are also used in chemical storage tanks, armored panels, civil structures, air conditioning ducts, furniture, and sports equipment [8]. The commonly used thermosetting matrix includes the following:

- Epoxy: Epoxy resins are widely used for their exceptional mechanical properties, adhesion, and resistance to chemicals. They are often used in aerospace, automotive, and construction applications [19].
- Polyester: Polyester resins are known for their ease of processing and are commonly used in boat hulls, automotive parts, and laminates [20, 21].
- Vinyl Ester: Vinyl ester resins offer good corrosion resistance and are suitable for chemical storage tanks and pipes [22, 23].
- Phenolic: Phenolic resins are highly heat-resistant and find use in aircraft components, high-temperature insulation, and brake components [24, 25].

1.4.2 Thermoplastic Polymer Matrix

Thermoplastic polymers consist of long, interconnected chains of molecules and are often referred to as thermosoftening plastics [18]. These composites have carved out a niche for themselves owing to their ease of processing, consistent quality, robust damage resistance, and reduced environmental risks. They are being employed in various sectors, including automotive, aviation, packaging, and refrigeration [8]. In numerous manufacturing procedures, thermoplastic matrices undergo heating and shaping via techniques like molding, extrusion, injection, or thermoforming, followed by a cooling process to uphold the intended structure of the end product. Importantly, this process is reversible, allowing for reshaping if needed [26]. Thermoplastic polymer matrix materials offer various benefits that make them advantageous for various applications. Some of the key merits of thermoplastic polymer matrix materials include recyclability, ease of processing, short processing times, a wide range of material options, chemical resistance, good impact resistance, high strength-to-weight ratio, flexibility and toughness, good electrical insulation properties, suitable for 3d printing, ductility, thermal conductivity control, and many more [27–29]. The choice of matrix material should consider the specific requirements of the application to ensure the best performance. The commonly used thermosetting matrix includes the following:

- Polyethylene (PE): PE-based matrices are used in applications requiring low cost, chemical resistance, and electrical insulation [30, 31].
- Polypropylene (PP): PP matrices are lightweight and have good chemical resistance. They are used in automotive and consumer goods [32, 33].
- Polyamide (Nylon): Nylon is renowned for its exceptional strength and durability, which makes it well-suited for various uses, including gears, bearings, and structural components [34].
- PC: PC matrices offer transparency and impact resistance and are used in applications like eyewear lenses and electrical enclosures [26, 35, 36].
- Polyether Ether Ketone (PEEK): PEEK is a high-performance thermoplastic with exceptional heat and chemical resistance commonly used in aerospace and medical devices [26].

1.5 Reinforcement Materials

The reinforcement serves as the structural backbone, providing mechanical strength in terms of tensile strength and rigidity. The reinforcements can range from elongated particles to continuous strands and are filamentary, either organic or inorganic in nature. This transition from fine particles to continuous fibers is crucial [37]. The predominant choice for reinforcement is E glass fiber, constituting over 95% of applications. Additionally, aramid fiber, like Kevlar, holds considerable interest [38, 39]. In general, the fibers perform effectively in traction in a composite structure (anisotropic). However, compared to metallic structures (which are isotropic), these composites display relatively lower performance in compression and notably weaker shear resistance. Typically, these reinforcements are utilized as fibers or modified variants.

1.5.1 Glass Fibers

At present, glass fibers dominate as the primary choice for reinforcement in advanced composite materials across a wide array of industrial applications [40]. Glass fibers play a pivotal role as the fundamental strengthening component in the widespread application of high-performance composite materials.

1.5.2 Phenolic Fiber

The industrial polymer produced under the trade name KYNOL is recognized for its outstanding thermal performance and commendable dimensional stability.

1.5.3 Polybenzimidazole (PBI) Fiber

PBI stands as a highly efficient fiber known for its cutting-edge properties within polymer composite, useful in the aerospace, automobile, and wind power industries [41]. Referred to as PBI fiber, it is crafted by spinning a poly(2,20-(m-phenylene)-5,50-bibenzimidazole) in dimethylacetamide solvent, resulting in its unique characteristics.

1.5.4 Aramid Fibers

Presently, high-performance polymeric composite, bolstered by aramid fiber reinforcement, demonstrates remarkable economic viability in industrial sectors. These sophisticated materials boast exceptional toughness, outstanding impact resistance, low density, and an extended lifespan [42–44]. Aromatic polyamide fibers, with KEVLAR being the most renowned, are created through a polycondensation methodology involving para-phenylene diamine and terephthalic acid chloride, conducted in N-methylpyrolidone solvent [26].

1.5.5 Carbon Fiber

Carbon fibers play a significant role in crafting composite materials and find extensive applications across various industries, including space construction, aeronautics, aircraft, and automobiles [45, 46]. Renowned for their outstanding mechanical and thermal resistance properties, carbon fibers exhibit remarkably high compressive and tensile strength as well as exceptional rigidity. Derived from polyacrylonitrile and processed through carbonization and subsequent graphitization, carbon fibers are widely recognized as the premier choice in fiber materials.

1.6 Filler Materials

Filler refers to an inert material incorporated into the base polymer, allowing for significant modifications in electrical, mechanical, or thermal properties, enhancing the appearance of surface, or simply reducing the total cost of the resulting composite [26, 47]. Various fillers are employed in polymer composites to modify and enhance their properties. In numerous research endeavors, the proportion of filler ranges typically from 4 to 5% based on weight [48]. The selection of filler relies on the particular application requirements, cost considerations, and the desired properties of the eventual composite material [49].

1.6.1 Organic Fillers

Organic fillers are materials derived from living organisms or carbon-based compounds and used in polymer composites to improve specific properties. It includes natural fibers, cellulose fillers, vegetable fibers, starch-based fillers, chitosan, and many more [48].

1.6.2 Mineral Fillers

Mineral fillers are inorganic substances utilized to improve a range of properties for polymer composites. These are frequently employed because of their abundant natural availability, contributing to cost savings in the production of composite products, and their non-toxic nature [47]. These include carbonates, silica, alumina, clay, talc, and various oxides. Different mineral fillers offer unique advantages and can be tailored to meet the needs of specific applications.

1.6.3 Metallic Fillers

Metallic fillers consist of metals or metallic compounds that are incorporated into polymer composites to augment specific properties. Metal-filled polymer composites offer advantages such as low specific weight, high resistance to corrosion, flexibility, and cost-effective processing methods. These composites provide a wide range of options for modifying their properties [50]. Adding metallic powders such as copper, aluminum, and zinc imparts electrical or thermal conductivity to plastic materials. Iron enhances resistance to abrasion, while lead offers shielding against radiation and absorbs sound within dense materials [26].

Various other additives are also utilized to enhance the physical characteristics, environmental stability, and rheological behavior of the polymers. These include lubricants, plasticizers, and many more. Sabirneeza et al. synthesized poly(vinylalcohol-leucine) (PVAL) composite-based corrosion inhibitor and studied its performance on mild steel in 1 M HCl. The findings revealed that PVAL worked as a mixed-type inhibitor, demonstrating a high inhibition efficiency of 95% at the optimum concentration of 0.6 wt% [52]. A remarkable improvement of 628 times in the wear resistance of epoxy/graphene composite was observed at 5 wt% loadings, rendering it well-suited for applications in electronics, marine, and aerospace sectors [58].

The following table (Table 1) summarizes the significant advancements in polymer properties achieved through composite forms. The upcoming sections emphasize diverse methods for synthesizing polymer composites and explore their wide range of application areas.

2 Methods of Synthesis

2.1 Melt Intercalation

Melt intercalation is the conventional and widely accepted method for producing thermoplastic polymer nanocomposites. This process includes heating the matrix phase to elevated temperatures, introducing the filler, and subsequently blending the material to ensure even dispersion of filler in the matrix, as shown in Fig. 3. One of its advantages is its environmentally friendly nature, as it doesn't involve the use of solvents [61]. It is the preferred method for producing clay/polymer nanocomposites with thermoplastics or elastomeric polymeric matrix. This method aligns well with existing industrial methods like injection molding and extrusion [62]. The primary benefit of this approach is its lack of toxic substances. However, a drawback emerges with the limited dispersion of the filler in the matrix, particularly at higher filler concentrations. This is due to the elevated viscosity of the composites [63]. Maiti et al. described a process of preparation of a mixture of Polycaprolactone (PCL) and multi-walled carbon nanotubes (MWCNTs) through melt blending. Subsequently, they synthesized a nanocomposite of PC and ε-PCL-MWCNT. A PCL-MWCNT masterbatch containing 3.5 wt% of MWCNT was created at 65 °C and 60 rpm using a mixer. This mixture was then further blended with PC at 280 °C and 60 rpm for an additional 10 min. A uniform dispersion of carbon nanotubes (CNTs) at minimal concentrations was observed in scanning electron microscope analysis. No chemical alteration of CNTs was necessary since the percolation threshold was achieved at just 0.14 wt%, indicating the successful formation of an interconnected network even at low CNTs loading [64]. Lee et al. prepared biodegradable nanocomposites by blending a polymer resin and layered silicates via the melt intercalation method. Initially, a blend of organoclay and polymer chips (GREENPOL) was prepared by employing a mechanical oscillator. Subsequently, this mixture was dried at 80 °C, and the nanocomposites were then processed through melt compounding using a twin-screw extruder, varying the organoclay content. With an increase in the clay loading, there was an improvement in the storage modulus, accompanied by the observation of a transition toward solid-like behavior. Moreover, there was an increase in the shear

Table 1 Advancements in polymer properties through composite forms

Polymers Composite	Loading	Remarks	References
Nylon 12/ IF-WS_2	2 wt%	The composites experienced a 27% rise in tensile property and a 28% improvement in bending strength	[51]
PVAL	0.6 wt%	The composite exhibited over 95% efficiency in inhibiting corrosion at an optimum concentration compared to the untreated metal	[52]
Epoxy/ WS_2-PEI	0.25 wt%	The fracture toughness exhibited an 82.98% increase, and the flexural strength saw a rise of 65% when compared to the pure epoxy	[53]
PVP/ $Zn_{1-x}Sn_xS$	1 wt%	The polymeric composite films demonstrate improved refractive index (n) and optical conductivity ($\sigma_{opt.}$) compared to the plain films	[54]
Epoxy/ GBN	5 wt%	The composite exhibited a substantial increase (~140%) in thermal conductivity. It also displayed elevated electrical resistivity of 3.05×10^{12} Ω•cm and minimal dielectric loss with tanδ less than 0.08	[55]
PVDF/ BT@BN	5 wt%	High electric breakdown strength (E_b ≈580 kV/mm) and notable discharged energy density (U_d ≈17.6 J/cm^3), surpassing the PVDF film by 1.76 and 2.8 times, respectively	[56]
PDMS/ CB-GF	8 wt%	The composite displays superior characteristics, with thermal conductivity 222% higher and storage modulus 40% greater than pure PDMS	[57]
Epoxy/ Graphene	5 wt%	The composite displayed a wear resistance 628 times greater than pure epoxy at 10 N, making it suitable for aerospace, electronics, and marine components	[58]
PLA/IL/ APP	3 wt%	The composite achieved notable flame retardancy (limiting oxygen index: 27.2, UL-94: V-0 grade). Furthermore, the elongation at the break rose from 8.5% in PLA to 204.6%	[59]
PU/GN	3 wt%	Nanocomposite films exhibited a 30% decrease in gas permeability, enhancing helium gas barrier properties. Additionally, their improved weather resistance led to reduced photooxidation and carbonyl index	[60]

IF-WS_2—fullerene-like tungsten disulfide, WS_2-PEI—branched polyethyleneimine-functionalized WS_2, PVP—polyvinyl pyrrolidine, GBN—hybrid graphene and boron nitride nanoparticle, PVDF—poly(vinylidene fluoride), BT@BN—$BaTiO_3$ nanoparticles embedded in boron nitride nanosheets, PDMS—polydimethylsiloxane, CB-GF—carbon black-graphene foam, PLA—poly(lactic acid), IL—ionic liquid (tetrabutylphosphonium), APP—ammonium polyphosphate, PU—polyurethane, GN—functionalized-graphene

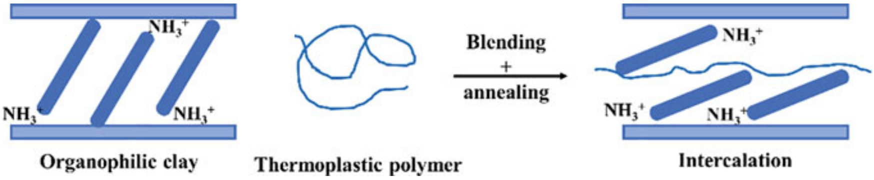

Fig. 3 Schematic representation of melt intercalation process [66]

viscosity of the nanocomposite, accompanied by the observation of shear-thinning behavior [65].

2.2 Solution Mixing/Solution Intercalation/Solution Blending

Solution mixing is one of the simplest techniques for creating polymer composites. The method comprises the following three steps:

- Dispersion of filler.
- Integration of the polymer.
- Elimination of the solvent through distillation or evaporation [63, 67].

In this procedure, nanofillers are initially immersed in a solvent, such as toluene, H_2O, or $CHCl_3$. The polymer and nanofillers are further blended in the solution, resulting in the intercalation of polymer chains and solvent displacement. After the removal of the solvent, the exfoliated structure persists, leading to the formation of polymer nanocomposites, as shown in Fig. 4 [62]. In contrast to melt intercalation, the driving factor in this process is the increase in entropy achieved by the removal of the solvent [61]. In the solution intercalation procedure, typically, high-velocity shear mixing, stirring, or ultrasonication is done to blend the filler suspension in the polymeric solution [68]. The first graphene-based nanocomposite was developed using an ultrasonic-based solution intercalation technique [69]. This method has found widespread application because of its efficiency in distributing nanofillers, regardless of the polymer's polarity, although its success relies on the harmony between the polymer and reinforcements concerning solvent compatibility. Despite the numerous merits of solution mixing, effectively removing solvents poses a considerable challenge, hindering its broad industrial adoption. The drawbacks include the expensive nature of solvents and the environmental impact of their disposal, which can impede scaling up and the ultimate adoption of this process by the industry. Moreover, while solution mixing achieves satisfactory dispersion in its liquid state, intricate details of each element or processing variables (like solvent type and quantity, mixing duration and velocity, sonication, etc.) profoundly impact the final results of the process [68]. Solution mixing can offer advantages at the laboratory scale since it doesn't necessitate costly equipment, and although it entails several steps, the operational procedures

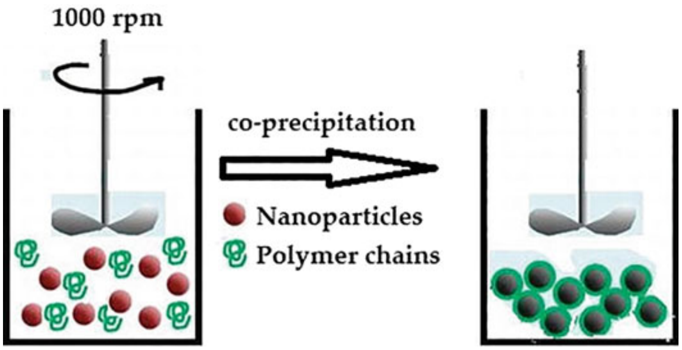

Fig. 4 Schematic diagram for the solution blending process. Reprinted with permission from ref. [71]

are relatively straightforward. This method is amenable to use at moderate temperature conditions and is well-suited for generating numerous small-sized specimens [70].

2.3 *In-Situ Polymerization*

In the method of in-situ polymerization, the typical process entails combining nanomaterial with a pure monomer or a monomer solution, followed by initiating polymerization while the nanomaterials are dispersed in the mixture (Fig. 5) [72]. This approach is exceptionally successful in achieving a consistent dispersion of carbon-based fillers within the matrix, leading to a robust interplay between the matrix and the filler. In-situ polymerization has also been successfully employed in various graphene oxide nanocomposite systems [73]. This method holds particular significance in the creation of composites with polymers that are either insoluble or thermally unstable as matrix materials. This is due to the inability of these matrices to dissolve in solvents suitable for solution mixing or to fuse during melt mixing. In comparison to the previously mentioned methods for preparing nanocomposites, this technique yields the most superior dispersion of the filler [68]. In-situ polymerization offers several distinct advantages. Firstly, it enables the synthesis of nanocomposites using both thermoplastic and thermoset matrices. Additionally, it allows for the grafting of polymers onto the filler surface, typically enhancing the properties of the resulting composite. This method can also achieve partially exfoliated structures because of the effective dispersion and intercalation of fillers within the polymer matrix [61]. The key challenge for achieving well-dispersed particles within the resulting polymer is ensuring effective dispersion of the particles within the monomer, as sedimentation processes in monomers can occur rapidly [73]. Avella et al. developed a novel abrasion-resistant nanocomposite using a poly(methyl methacrylate)

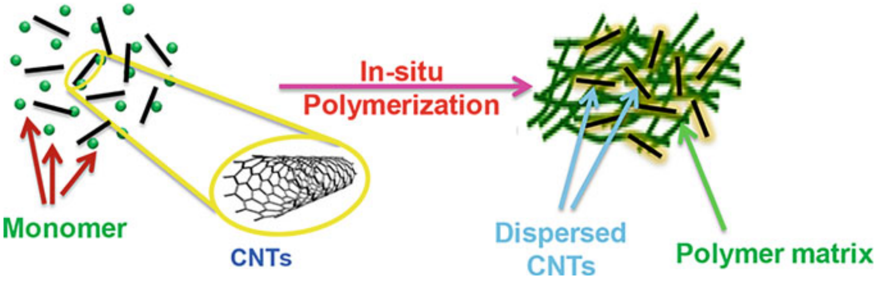

Fig. 5 Schematic route of in-situ polymerization process. Reprinted with permission from ref. [76]

matrix and calcium carbonate ($CaCO_3$) nanopowder through an in-situ polymerization method. They examined how the nanopowders affected the chemical and physical properties of the polymer matrix by conducting analyses of thermal, morphological, and mechanical characteristics [74]. Allen et al. synthesized composite films and fibers of single-walled carbon nanotubes (SWCNT) and conductive polymer through an in-situ polymerization method. The results indicate an improved in-situ polymerization workability of SWCNT/conjugated polymer gels, enabling the creation of transparent electrodes and composite fibers [75].

No single technique meets all requirements perfectly. Consequently, there have been attempts to combine methods, such as employing a blend of solution processing and melt mixing, in-situ polymerization coupled with solvent processing, or in-situ polymerization combined with melt processing.

3 Applications of Polymer Composites

Polymer components are progressively replacing metals in various applications, including structural elements, housings, flexures, and bearings, especially in the automotive industry, in order to reduce weight [77]. Reinforced polymer composites find extensive utility across diverse applications due to their ability to fulfill a broad spectrum of often intricate performance requirements. Most of these materials incorporate some form of glass or carbon fiber reinforcement, which has historically delivered the most substantial enhancements in mechanical properties to the composites [78]. Due to its lightweight nature and exceptional mechanical properties, polymer composites are employed as structural components in imaging devices. The extensive utilization of composite materials across industries is attributed to their favorable strength-to-density and hardness-to-density ratios [79].

3.1 Construction Industry

In recent decades, the construction industry has encountered new challenges due to the increasing demand for infrastructure projects, coupled with the depletion of natural resources like water, limestone, and clay. To address the issue, there is a growing need to explore alternative materials to create innovative construction materials. These materials should not only enhance structural performance but also mitigate problems related to poor durability, ultimately reducing repair costs. Consequently, the construction industry, which is a prominent consumer of composite materials, has witnessed a historical alliance with versatile polymers. Polymer concrete composites represent a groundbreaking strategy for advancing and addressing environmental concerns within the domains of raw material extraction, formulation of mix ratios, and the establishment of construction standards for both the construction and restoration of concrete structures. Polymer concrete, as a building material, is the result of polymerizing a blend of monomers and aggregates. The polymer matrix effectively unites the aggregates, forming a cohesive material. The inception of polymer concrete was conceived with the primary aim of serving as an alternative to traditional cement, particularly tailored for specific applications in the construction industry [80]. Unreinforced polymer composites have found application in various non-load-bearing roles within construction, adorning trimmings, kitchenware, vanities, and cladding [81]. However, the past decade has seen a focused endeavor to introduce reinforced composites into the construction sector for pivotal load-bearing functions. Polymer composites have historically been embraced within the construction realm, gracing them with their utility in non-critical assignments such as baths, vanities, cladding, and decorative elements [82]. Through a synergistic reaction, the polymer and cement interact to form an exclusive microstructure exhibiting distinct properties. The polymer plays a pivotal role in these materials, serving three primary functions as follows:

(1) Acting as a rheological aid by coating individual cement particles, thus diminishing interactions among them.
(2) Filling pores and voids between unreacted cement grains.
(3) Engaging in chemical interactions with the hydration products of cement, resulting in the formation of essential microstructural components known as the interphase regions [83, 84].

In recent times, FRP composite materials have experienced a surge in consideration within the construction sector for structural load-bearing roles. This reinforcement primarily involves the inclusion of fibers or other materials that enhance the material's strength, often in one or more directions. Glass, carbon, basalt, and aramid fibers are regarded as the most effective options as reinforcements in structural engineering. Carbon, glass, and aramid fiber composites are frequently utilized in the construction of building structures. These composites have proven their mettle as a compelling and competitive choice for renovating and fortifying existing civil structures, often replacing conventional steel within reinforced concrete and, albeit

Fig. 6 First FRP bridge in Ginzi, Bulgaria. Reprinted with permission from ref. [89]

to a lesser extent, in the creation of new civil edifices [85]. Like in various other applications of FRP composites, their utilization in bridge construction is on the rise. This increasing use can be attributed to four pivotal advantages as follows:

(1) Exceptional mechanical properties enable weight reduction owing to a favorable strength-to-stiffness-to-density ratio.
(2) Strong resistance to corrosion, enhancing the overall durability of the structure.
(3) Minimal maintenance requirements, leading to cost savings and reduced upkeep efforts.
(4) Capability to shape and mold intricate geometries and forms for bridge components and structures.

These benefits serve as catalysts for the adoption of FRP composites in crafting various components of bridges and even in the creation of large-span structures. The initial efforts to introduce FRP composites into the bridge construction industry date back to the mid-1970s [86]. One of the early examples of a road bridge constructed using FRP composites is the Ginzi Highway bridge (shown in Fig. 6), erected in Bulgaria from 1981 to 1982 [87]. This bridge featured a Glass-FRP slab manufactured as a single element using the hand lay-up technique, and it had a span of 10 m [88].

3.2 Automobile Applications

PMCs are extensively utilized in the automotive industry due to their lightweight properties and cost-effectiveness. The mechanical attributes of PMCs play a crucial role in vehicle design, enabling them to fulfill various criteria, such as reducing vehicle weight, thereby enhancing fuel efficiency and reducing exhaust emissions, consequently contributing to a reduction in air pollution. A frequently employed composite material in the automotive sector consists of a polymer matrix reinforced with whiskers or fibers. The automotive industry's first use of PMCs dates back to 1953 when the Chevrolet Corvette introduced a fiberglass body, marking the initial application of PMCs in the automotive field [79]. Over the last decade, European car manufacturers and suppliers have increasingly adopted natural fiber composites with both thermoplastic and thermoset matrices for diverse automotive applications. These include door panels, seat backs, headliners, package trays, dashboards, and interior components. Meanwhile, glass FRPs have demonstrated their ability to satisfy the structural and durability requirements of both interior and exterior automotive components [90]. The automotive industry has witnessed a substantial use of composites, particularly in manufacturing hybrid electric vehicles and electric vehicle batteries. These materials have contributed significantly to reducing vehicle weight and increasing driving range. In addition, sports cars and supercars have integrated polymer composites to enhance their capabilities and achieve significant reductions in emissions, meeting accepted standards. This shift has resulted in reduced overall vehicle weight, expenses, manufacturing intricacy, maintenance requirements, and extended lifespan while also allowing for flexible design with a focus on passenger safety. Polymer composites have demonstrated improved crash performance, a benefit particularly harnessed in Formula 1 racing cars, leading to a considerable reduction in life-threatening accidents associated with racing. Car manufacturers like Porsche and Mercedes-Benz are now utilizing polymer composites in the creation of high-end sports cars, particularly in the construction of passenger compartments [91]. Figure 7 shows the instance of polymer nanocomposites employed within the parts of the car.

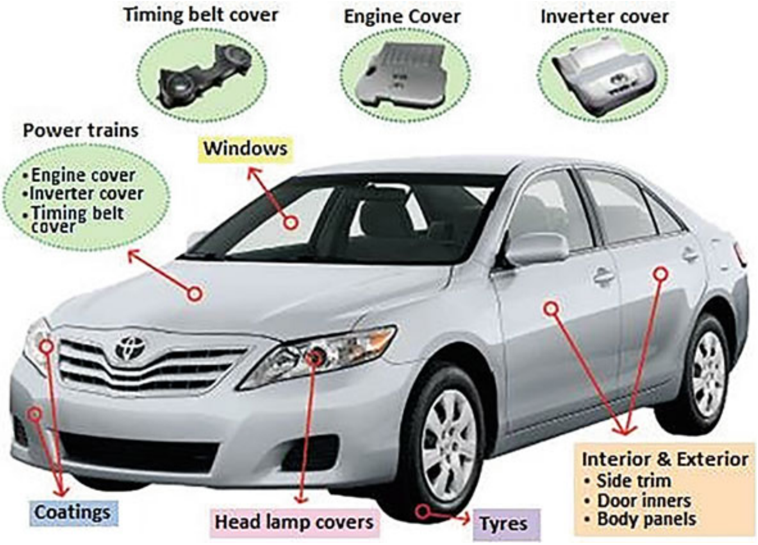

Fig. 7 Application of polymer nanocomposite parts. Reprinted with permission from ref. [92]

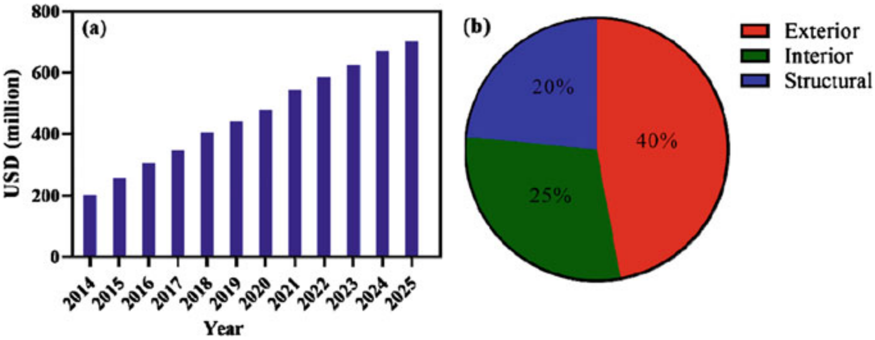

Fig. 8 **a** The market revenue for PMCs in the United States from 2014–2025. **b** The global utilization pattern of PMCs across various automotive components. Reprinted with permission from ref. [93]

Over the past few decades, there has been a consistent and significant increase in the revenue generated from using PMCs in the automotive sector, as depicted in Fig. 8a. An interesting observation from Fig. 8b is that a substantial proportion, around 65%, of these PMCs has found application in both the exterior and interior components of automobiles. According to a market report, the evaluation of the automotive polymer composite industry in 2014 amounted to USD 200 million, and there is a strong indication that this figure is projected to grow to USD 700 million by the year 2025 [93].

3.3 *Electronics and Communications*

As information technology advances rapidly, exemplified by the advent of 5G, the global landscape is undergoing a profound transformation driven by digital technology. Consequently, there is a growing need for everything to be "measurable" and "digital," as conventional rigid electronic devices relying on inorganic materials, semiconductors, and metals do not adequately meet the emerging requirements for flexibility, expansiveness, and wearability [94–96]. In response to this challenge, flexible electronics have witnessed a surge in popularity in recent years. Within this realm of flexible devices, polymeric composites assume a pivotal role owing to their versatile and adaptable features [97–99]. Primarily, in contrast to conventional manufacturing methods, polymeric composites can be strategically tailored using cost-effective techniques. Moreover, the chemical structures of polymers and their composites can be intelligently tailored to suit a broad range of applications. In addition, certain composites exhibit exceptional biocompatibility and stability in vivo, thus bestowing them with the ability to monitor health in complex biological contexts. Consequently, polymer composites have become indispensable materials in the realm of flexible electronics [100, 101]. The diagram presented in Fig. 9 illustrates the application of polypyrrole (PPy)-based composite in the domain of flexible electronics.

The proliferation of highly integrated circuitry in electronic devices has led to the generation of unwanted EM radiation, interfering with neighboring devices and causing malfunctions. Therefore, managing EM radiation has become a significant challenge in various sectors, including electronics, communications, military, and medical instruments. To mitigate the adverse effects of unwanted EM radiation, EM shielding compounds are indispensable. Extensive research has focused on the advancement of polymeric materials that provide inherent flexibility, ease of processing, resistance to chemicals, scalability, and lightweight characteristics. Additionally, shielding materials based on polymers offer benefits as compared to metal-based alternatives, as they can primarily shield electromagnetic waves through absorption. This renders them especially appealing for uses like incorporating camouflage and advanced stealth technology. Intrinsically conducting polymers, such as polyaniline and PPy, are the preferred choice for achieving effective Electromagnetic interference (EMI) shielding. Their good conductivity can be significantly enhanced through doping. This can be achieved through the appropriate addition of magnetic and electrically conducting fillers into the matrix. Notably, carbonaceous materials like CNTs, graphene, carbon black, and graphite fibers, as well as metallic structures like metal nanowires and nanoparticles, have been the primary choices for conducting fillers. These nanomaterials and their composites have demonstrated excellent EMI shielding and also found applications in solar cells, lithium-ion batteries, supercapacitors, electrochemistry, catalysis, sensors, improved mechanical properties, and numerous other potential uses [103].

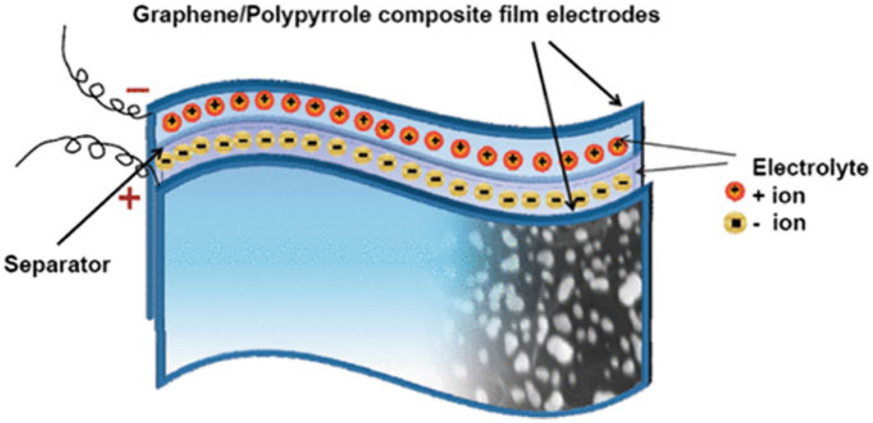

Fig. 9 A diagrammatic representation illustrating the structure of flexible supercapacitors based on Graphene/PPy composite. Reprinted with permission from ref. [102]

3.4 Marine Applications

In recent decades, the marine industry has witnessed widespread adoption of advanced composites owing to their exceptional engineering properties. The key factors driving this surge in usage across various marine sectors include reductions in weight and costs, as well as a commitment to environmental sustainability [5]. The integration of advanced composites marked a significant milestone in the boat and vessel manufacturing industry. This technology has empowered manufacturers to enhance product quality, resulting in rigid yet lightweight structures that contribute to improved sailing performance and longevity. The reduced weight brings advantages such as increased cargo capacity, fuel efficiency, reduced inertia, enhanced ship stability, and buoyancy [104]. The initial use of FRP composite materials in the marine sector was observed in the construction of boats shortly after World War II. A significant portion of maritime vessels is constructed using composites that include glass-reinforced polyester and advanced FRP materials, often incorporating carbon. They are commonly used for high-performance structural applications [105]. Recreational boats, military vessels, and even helicopter landing platforms situated in the middle of the ocean utilize these materials [106]. In the offshore sector, composites are used for various purposes, including repairs, such as submerged structures on spar platforms and pipes as well as in the floating platform components, construction of gas pipelines, and supporting engineering framework. Their suitability in offshore applications stems from their low weight, impressive specific mechanical properties, and resistance to the harsh seawater environment, making composite materials a viable substitute for metals [104]. Mouritz et al. [107] conducted a series of studies aimed at comparing the weight, structural performance, and cost of large patrol boats constructed from different materials, including steel, aluminum, and sandwich composites. Their findings indicated that when utilizing glass-reinforced plastic sandwich composite material, the structural weight of a boat could be reduced by 10% compared to an aluminum boat, and an even more significant reduction of 36% could be achieved in comparison to a steel boat of similar size. Furthermore, the research highlights the effectiveness of hybrid composites in maintaining essential mechanical properties required for prolonged and efficient performance within the marine industry. Notably, the hybrid glass-carbon reinforced polymer composite (GCG2C) exhibits an impressive flexural strength of 462 MPa while displaying minimal water absorption tendencies. In addition, a combination of flax and carbon fiber composites, used as a substitute for aluminum 6061 in structural materials, has shown remarkable improvements. This alternative offers a substantial 141% enhancement in vibration-damping properties and an impressive 252% boost in tensile strength, all while reducing weight by 49%. Moreover, the integration of reinforcements such as jute and carbon fibers in hybridized composites not only contributes to improved vibration-damping properties but also aligns with economic and environmental sustainability goals [5, 108]. An example in Fig. 10 is a Carbon-FRP propeller for application as a podded propulsion unit, which is manufactured using a hand lay-up process [109].

Fig. 10 Carbon fiber propeller fabricated through a hand lay-up process. Reprinted with permission from ref. [109]

Aerospace

Polymer composite materials have become increasingly prevalent in the aerospace industry, with up to 40% of modern airframes being constructed from these materials. The use of composites is expected to continue to grow due to ongoing advancements in technology [110]. Reducing weight, cutting costs, and ensuring radiation protection are key priorities in this sector. The reduction in weight is especially important as it impacts various factors, including fuel efficiency, velocity, number of assembled components, and others. Additionally, the implementation of nanofiller-reinforced polymer matrices has been investigated to enhance radiation shielding capabilities when compared to traditional metal alternatives. The capability of polymer composites to provide effective shielding is attributed to their insulating features and the opportunity to include non-toxic, high-Z fillers, thereby enhancing protection against X-rays. These polymer composites are applied in various components, including aircraft wing boxes, aircraft brakes, blades, fittings, window frames, rotors, brackets, bulkheads, fuselages, airframes, vertical fins, and tail assemblies [5]. In the aerospace and aeronautical fields, where safety and reliability take precedence over cost, the adoption of FRP composites has rapidly gained prominence. When seeking a unique combination of safety, reliability, lightweight characteristics, strength, and efficiency, polymer-reinforced composites emerge as the unparalleled choice [110]. As early as 1983, airbus became the first commercial aircraft manufacturer to incorporate composite materials into the design and construction of the rudders for its A300 and A310 aircraft. Carbon fiber is generally the predominant polymer composite material used in aerospace applications. Polymer composites are extensively utilized in the Eurofighter jet for constructing its wings, fuselage, flaperons, and rudder, with approximately 40% of the structural components of the Eurofighter being composed of carbon-FRP material [111]. Hybrid composites have also gained prominence in recent times, as research has revealed their improved mechanical properties, which are essential for aerospace applications. Hybrid composites, like kenaf/glass FRP composites, enhance the specific strength of aircraft. Additionally, the use of carbon fiber-reinforced silicon carbide in aircraft brake systems allows them to withstand temperatures as high as 1200 °C [5].

The Boeing 787 (Fig. 11) made aviation history by becoming the first commercial jet aircraft predominantly constructed from composite materials. This innovative approach is particularly evident in the main structure and fuselage of the Boeing 787, surpassing the use of composites in any previous Boeing commercial aircraft. The Boeing 787 is distinguished by its remarkable composition, with composites accounting for a substantial 80% of its volume. When considering the weight distribution, the materials consist of 50% composites, 20% aluminum, 15% titanium, 10% steel, and the remaining 5% comprised of various other materials. The key to this groundbreaking design was that nearly half of the fuselage was crafted from carbon-FRP and other composite materials. This revolutionary approach, when compared to conventional aluminum designs, results in an average weight reduction of approximately 20% [112, 113].

Biomedical

The substantial rise in demand for medical products utilizing biomaterials and tissue engineering has spurred significant growth in biomedical research over the last two decades [114–116]. These biomaterials play a crucial role in the development of various biomedical devices, ranging from hydrogel contact lenses to polymer stents, knee and ligament implants, surgical adhesives, polymer vascular grafts, steel joint and hip replacements, artificial heart valves, ceramic dental implants, polymer barrier films, polymer sutures, and porous dialysis membranes, among others. As per the comprehensive global industry analysis, the biomaterials market surpassed USD 94 billion in 2018, with projections indicating it is set to surpass USD 256 billion by 2025. An intriguing category of biomaterials, polymer-based composites, is currently

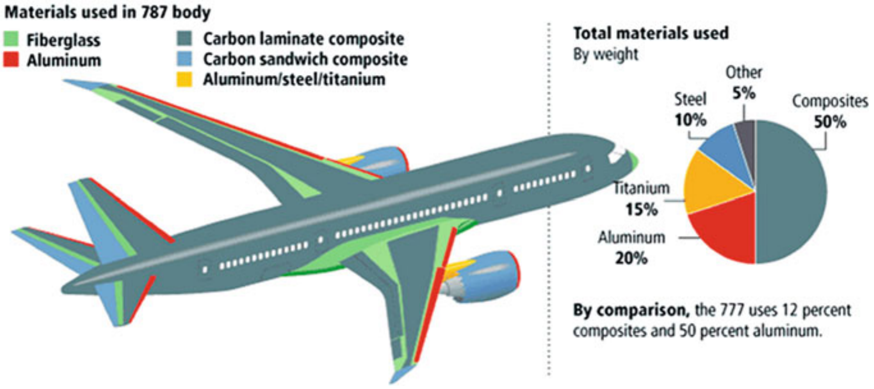

Fig. 11 The comprehensive allocation of composite materials employed in Boing 787 aircraft. Reprinted with permission from ref. [113]

extensively employed in biomedical applications (Fig. 12) due to their exceptional mechanical and physical characteristics [117]. Furthermore, polymer-based nanocarriers receive the most attention among organic-based photothermal carriers for cancer therapy [118]. It is worth noting that polymer-based nanofibrous materials find application in numerous biomedical fields, including tissue engineering for oral tissues, blood vessels, bones, and wound dressing [119]. Their applications span various fields, encompassing wound dressing, dental practices, medical devices, blood vessel treatments, tissue engineering, oral tissue treatments, antimicrobial materials protein immobilization, surgical implants, drug delivery systems, regenerative medicine, and bone therapy. Within the biomedical realm, natural polymers such as chitosan, collagen, pectin, psyllium, agar, guar gum, starch, and cellulose, as well as synthetic counterparts like polyglycolic acid, polyester amides, PCL, polyamide, PLA, and poly lactic-co-glycolic acid, are widely used predominantly employing fibers as their primary reinforcement mode [5]. In the realm of bio applications, polymer composites offer several benefits, including cost-effectiveness, utilization of readily available natural and synthetic matrices, and tunable fabrication techniques [120]. Various fillers possessing bioactive or non-bioactive properties present opportunities for crafting appropriate scaffolds or implants in the field of regenerative medicine and tissue engineering applications. Modern techniques involving polymer composites typically require refinement to fine-tune the structure needed for specific applications. Polymer composite scaffolds have demonstrated high cell adhesion, biodegradability, and biocompatibility with exceptional bioactivities in terms of tissue formation, stimulation, survival, function, and antimicrobial properties in both in vitro and in vivo experiments [117].

Polymer Composites serve as integral components in a diverse array of medical devices, including MRI and CT scanners, X-ray couches, surgical tables, mammography plates, target tools for surgeries, wheelchairs, and prosthetics. Examples of these applications are outlined below.

Polymer nanocomposites, incorporating CNTs or TiO_2 nanotubes, contribute to the accelerated healing of fractures by serving as a “scaffold” that directs the growth of new bone [122]. The exploration of nanocomposites in diagnostics and therapy is underway, with one example being the integration of magnetic nanoparticles and fluorescent nanoparticles in composite particles. These particles exhibit both magnetic and fluorescent properties, enhancing tumor visibility in pre-surgery MRI tests and potentially aiding surgeons in better-visualizing tumors during surgical procedures. Polymer composites find extensive use in biomedical applications, serving in both soft tissues like skin and hard tissues such as bone. The utilization of both synthetic and naturally degradable polymer composites is prevalent in creating scaffolds for bone repair, leveraging their exceptional biological and mechanical attributes [123].

Researchers are employing biocompatible polymer composites in the realm of skin regeneration these days. Polymeric materials play a crucial role in drug delivery systems due to their high suitability and adaptability. Specifically, polymer-based hydrogels serve as carriers for various drug molecules, including antifungal, antibiotic, and anticancer drugs. These hydrogels not only act as protective barriers at wound sites, expediting the healing process, but also contribute to tissue engineering