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Overview and Present Status of Reinforced Polymer Composites

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1.1 Introduction

Humans have been using a number of materials to improve their living standards since ages. In fact, the progress of human civilization has been classified into three categories, popularly known as the Stone Age, the Bronze Age, and the Iron Age, on the basis of materials only. Looking at the current rate of demand and consumption of plastics, it would not be wrong if somebody categorizes the present age as "The Age of Plastics" or "Plastic Age". New materials form the foundation for new technologies and help in understanding nature. The most complex designs in the world can be of no use if suitable material is not used during the fabrication of products with that design. In actual realization of a design, the role of materials is quite indispensable. The limited availability of natural resources has forced material engineers to use materials in a more conscious manner. Therefore, material scientists and engineers are trying to optimize the use of materials in every possible field of application. In the present age, transportation industry is the biggest contributor of carbon footprints in the environment. Lower fuel consumption of automotive vehicles can lower the carbon footprints. In the quest for achieving low fuel consumption, transportation industry is leaning toward materials having high strength to weight ratio. Reinforced polymer composites (RPCs), also known as fiber reinforced polymer composites (FRPCs) are such promising materials for almost every industry looking for low weight and high strength materials [1]. The application spectrum of FRPCs has spread in almost every sector starting from engineered domestic products to the highly sensitive biomedical industry. FRPCs are not only just a replacement for conventional alloys but they also provide engineered properties. Rahmani et al. [2] fabricated the carbon/epoxy-based FRPCs with 40 wt% of fiber. This system of FRPCs was able to achieve a tensile strength of 2500 MPa, which is quite close to the tensile strength of steel. The authors concluded that fiber orientation was the most influencing factor among other factors, namely number of laminates and resin type. The authors suggested the use of ±35° angle of plies to obtain

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better tensile properties along with good flexural properties. Modification in the matrix material can enhance the overall properties of FRPCs. Islam et al. [3] modified the epoxy matrix by incorporating nanoclay and multiwalled carbon nanotubes (MWCNTs). The authors found significant improvement in the static and dynamic mechanical properties of the developed carbon fiber-based FRPCs. Cho et al. [4] enhanced the in-plane shear strength and shear modulus of carbon fiber reinforced epoxy composites by incorporating graphite nanoplatelets in the epoxy matrix using the sonication method. Increasing the volume fraction of reinforcement can increase the mechanical properties of the developed FRPCs. Aramide et al. [5] fabricated glass fiber/epoxy-based FRPCs with varying volume fraction of fibers from 5% to 30%. The authors found that the mechanical strength increased as the fiber volume fraction increased up to 30%. Treinyte et al. [6] fabricated poly (vinyl alcohol)-based pots. Forestry and wood processing waste was used as filler in the matrix. The authors claimed that the manufactured pots showed 45% lower water evaporation rate in comparison to regular peat pots.

Architecture of the reinforcement also affects the mechanical performance of developed FRPCs products. A range of reinforcement architectures is available in the market such as short fiber, unidirectional prepregs, 2D and 3D woven mats, braided mats, and knitted mats. Every architecture has its own merits and demerits – 2D woven mats show better in-plane mechanical properties but they lack in out-of plane properties while 3D woven mats offer better out-of-plane properties in comparison to others [7]. Erol et al. [8] investigated the effect of yarn material and weaving pattern on the macroscopic properties of FRPCs and concluded that weave pattern greatly influenced the tensile and shear properties of the developed composites. Some authors [9] have even used 3D and 5D braided reinforcement for the development of FRPCs. The authors concluded that braided architecture affects the fracture mechanism in a significant way. Kostar et al. [10] used two-sided co-braided carbon and Kevlar hybrid reinforcement for the development of FRPCs and concluded that the tensile strength and modulus of hybrid reinforcement-based FRPCs were 13% and 80% higher than those with simple reinforcement. FRPs have evolved over a long time period as shown in Figure 1.1.

Environmental problems and difficulty in the recycling associated with synthetic composites have led to the development of biocomposites/green composites. Biocomposites are eco-friendly materials with adequate mechanical properties. Fombuena et al. [11] fabricated biocomposites using bio-fillers derived from sea-shell waste as reinforcement in bio-based epoxy matrix. The authors found impressive improvement in mechanical properties of bio-based epoxy when reinforced with bio-fillers. End of life (EOL) impact of synthetic fibers and polymers is negative to the environment. Duflou et al. [12] showed that low mechanical strength of flax fiber is an obstruction in the replacement of glass fiber but it can be used in many applications where high mechanical strength is not the primary requirement. Effect of moisture on the mechanical performance of natural fiber-based biocomposites is yet another concern while using biocomposites. Baghaei et al. [13] developed poly lactic acid (PLA)-based biocomposites and analyzed the moisture absorption behavior. The authors found that the moisture absorption characteristic of the developed composite

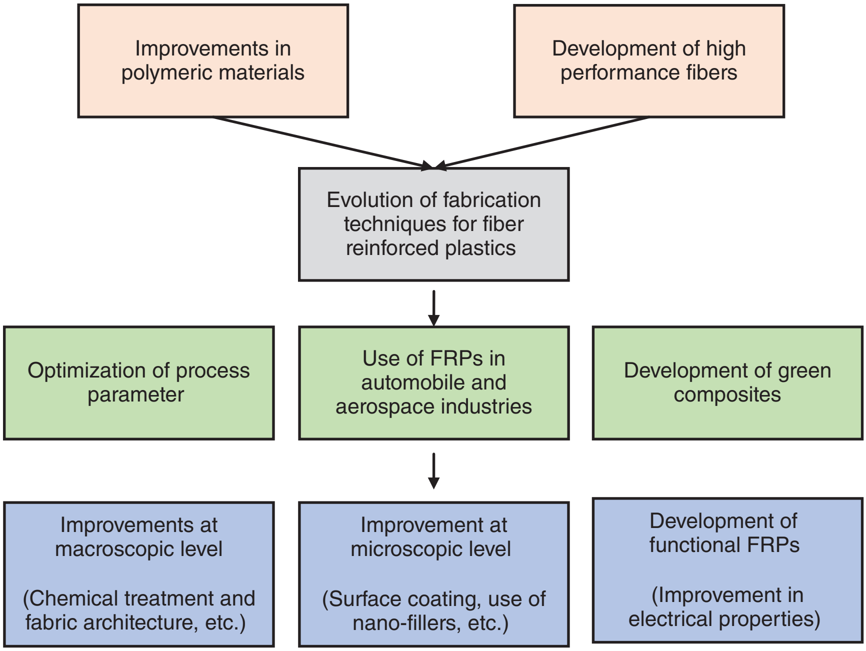

Figure 1.1 Development stages of FRPs.

was reduced when the reinforcement was used in the woven form instead of the nonwoven form.

Hybridization can improve the mechanical strength of green composites. Hassanin et al. [14] developed a biocomposite particle board using a mixture of wood particles and short glass fibers covered with an outer layer of jute fabric. The particle board showed excellent mechanical and physical properties in comparison to commercially available particle boards. Chaudhary et al. [15] hybridized the reinforcement and found improved mechanical and thermal properties of the developed biocomposites. The authors used three types of woven fibers mats, namely jute, hemp, and flax, as reinforcement in epoxy matrix.

Chemical treatment of fibers/surface modification of fibers is also a promising method for improvement in the mechanical properties of FRPCs. Alkali, acryl, benzyl, and silane solutions are commonly used for the treatment of fibers [16]. Asaithambi et al. [17] treated banana fibers before using them as reinforcement in PLA-based FRPCs. Banana fibers were first pretreated with 5% NaOH solution at room temperature for around two hours, and then the chemical treatment of the fiber was completed using benzoyl peroxide. Significant improvement in the mechanical properties developed with treated FRPCs was found in comparison to those developed with untreated FRPCs. Rahman and Khan [18] used ethylene dimethyl acrylate (EMA) for the surface modification of coir fibers along with UV treatment for the aging of fibers. The authors concluded that the mechanical properties of FRPCs developed using treated fiber were better than those of untreated fiber reinforced FRPCs.

1.2 FRPCs

FRPCs are multiphase materials comprised of natural/synthetic fiber as reinforcement and thermoset/thermoplastic polymer as matrix, resulting in synergistic properties that cannot be achieved from a single component alone. In general, reinforcement is in the form of long continuous fibers but they can be used in various other forms such as short fibers, fillers, or whiskers. The fibrous form of reinforcement is used in composite materials because they are stronger and stiffer than any other form [19]. Synthetic fibers (carbon, glass, aramid, etc.) can provide more strength than most of the metals along with being lighter than those materials. On the other hand, natural fibers are also being used in a number of structural as well as nonstructural applications due to the environmental problems associated with synthetic fibers. Matrix material, which is generally continuous in nature, protects the reinforcement from adverse environment and transfers the load to reinforcement from the point of application of load [12]. The matrix material holds the flexible reinforcements together to make it a solid. Matrix material is also responsible for the finish and texture of the composite material. The properties of composite materials depend on the dispersion and properties of the constituents and their interfacial interaction. Tailoring the properties of a material according to the requirement of application can be easily done in composite materials [20]. Table 1.1 shows the commonly used natural and synthetic polymers and fibers used as matrix and reinforcement, respectively.

1.2.1 Fabrication of Fiber Reinforced Composites

Fabrication methods of FRPCs still require a lot of attention in order to produce defect-free high quality products. Some unique features of primary and secondary processing of FRPCs are tabulated in Table 1.2.

Table 1.1 Matrix and reinforcement materials used in reinforced polymer composites.

Matrix	Natural	Synthetic
	Polysaccharides such as homoglycans, cellulose, chitin, chitosan, heteroglycans, such as alginate, agar, and agarose, carrageenan, pectins, gums, and proteoglycans, protein, peptides, and enzymes	Polyolefins, poly(tetrafluoroethylene) (PTFE), poly(vinylchloride)(PVC), silicone, methacrylates, aliphatic polyesters, polyethers, poly(amino acids), polyamides, polyurethanes, epoxy, polycarbonates
Reinforcement	Natural	Synthetic
	Animal-based – silk, wool, hair; Plant-based – bast fibers (jute, flax, ramie, hemp, kenaf, roselle, etc.), leaf fibers (sisal, banana, agava, etc.), seed, fruit, wood, and stalk fibers	Carbon, glass, Aramid/Kevlar, graphite, aromatic polyester fibers, boron, silica carbide

1.2.2 Present Status of FRPCs

RPC products such as pipes are being used in various adverse conditions such as in offshore and marine applications. These pipes are exposed to severe climatic conditions ranging from −40 to 80 °C [21]. Benyahia et al. [21] tested the mechanical properties of a filament wound glass/epoxy pipe of 86 mm diameter and 6.2 mm thickness. The authors estimated that there was degradation of mechanical properties at higher temperatures. Ellyin and Maser [22] investigated the effect of moisture at elevated temperature on the mechanical properties of glass fiber reinforced polymer (GFRP) composite tubes. At lower temperature, the ductility of the specimen was found to be decreased drastically and the stiffness was increased. Above the glass transition temperature, there was sudden degradation in the mechanical properties of composite pipes. In recent progress, shape memory alloy (SMA) wires are being incorporated into the FRPCs as reinforcement to increase the functionality of the developed composites such as shape recovery, high damping capacity, generation of high recovery stresses, and controlled overall thermal expansion. SMA wires not only improve the functionality of the FRPCs but also offer improved mechanical properties [23]. Paine and Rogers [24] concluded that the low velocity impact properties of FRPCs can be improved by incorporating SMA wires. Incorporation of just 2.8% volume fraction of SMA wires as reinforcement was able to increase the impact delamination resistance by 25% in comparison to the FRPCs without the SMA wire reinforcement. Pappada et al. [25, 26] fabricated hybrid glass fiber reinforced vinyl ester-based FRPC material and incorporated SMA wires in two forms, namely unidirectional SMA wires and knitted SMA wires. The authors assessed impact properties and found that FRPCs reinforced with SMA wires achieved higher impact properties than FRPCs with unidirectional SMA wires.

Polymer nanocomposites are also a relatively new class of materials. Nanocomposites are generally fabricated by incorporating one or more constituents of the size of the order of nanometers. These constituents are generally inorganic in nature and known as fillers, and not as reinforcement, due to their small size. Various researchers have reported impressive properties of nanocomposites such as high modulus and strength, high resistance to heat, and reduced flammability. However, effective dispersion of the nano-sized fillers throughout the polymer matrix is still a challenge, and moreover this dispersion controls and determines the physical, chemical, and mechanical properties of the developed FRPC products [27–29]. The authors have used an in situ approach to homogenize the dispersion of nano-sized fillers. In this approach, nano-fillers are directly synthesized with the polymer using some suitable precursor [30, 31]. Although the in situ approach provides controlled dispersion of nano-fillers, it involves complex procedures and processing steps along with expensive reactants [32, 33]. Various researchers used the ball milling method to fabricate nanocomposites. In this method, first both the constituents, polymer and nano-fillers, are mixed with each other in solid state using ball mills and then the mixture is melted to polymerize. Although the morphology of the fillers changes in the ball mill, this change positively affects the composites by enriching the filler compatibility with the polymer. The ball milling method is not just an alternative to ex situ

Table 1.2 Primary and secondary processing methods for FRPCs.

Processing	Fabrication technique	Features
Primary processing methods	Hand lay-up	Minimum infrastructural requirement; low initial capital requirement; only for thermosetting resins; lower production rate; and low volume fraction of the reinforcement
	Spray lay-up	Extension of hand lay-up technique; reinforcement in the form of chopped fibers only
	Compression molding	Use of heat and pressure both simultaneously; dimensionally accurate and finished products; process parameters need to be optimized; both thermosetting and thermoplastic polymers can be used; higher initial capital requirement compared to hand lay-up
	Injection molding	Reinforcement only in the form of short fibers; damage of fibers in barrel due to shearing action of screw. Highly accurate dimensions of the product; used for mass production
	Pultrusion process	Resin impregnated continuous fibers are passed through a heating die for curing; automated process used for continuous production; only products with constant cross-sectional area depending on the die can be manufactured
	Resin transfer molding	Liquid resin system is forced into the mold; high fiber volume fraction can be achieved. Good surface finish with minimum material wastage
	Filament winding	Continuous fiber strands as reinforcement; controlled fiber orientation; high production rate; high capital investment; not possible to produce female features of products and expensive mandrel
	Vacuum assisted resin transfer molding	Uses vacuum to ensure zero voids; superior quality composites using autoclave (a strong heating container that is used for applying heat and pressure at the time of curing of the composite laminates)
Secondary processing methods	Conventional machining	Drilling with twist drill is the most used conventional method to produce holes in laminates. Requires milling machine or drilling machine. Spindle speed, feed rate, and drill geometry are influential parameters. Delamination, fiber linting, and fiber pull-out are the most common defects
	Unconventional machining	Abrasive water jet (AWJ) reduces the thermal damage that could be generated in conventional machining. Laser beam (LB) cutting is also being used for holes generation in composite laminates. High energy input is required. Ultrasonic machining (USM) can also be used for hole making in the composite laminates

fabrication of FRPCs but is also an environment friendly and economical method to produce nano-filler reinforced FRPCs [34]. Some authors [35] have also used reinforcing metallic powders such as copper powder of 29.5 and 260 μm size in the polyvinyl butyral (PVB) polymer matrix to fabricate polymer composites. Fan and Wang [36] developed a transparent protective polymer composite material with lightweight property, which could be used against high speed impact loading.

The behavior and performance of FRPCs changes from application to application. FRPCs exposed to various tribological environments lead to the necessity to evaluate the tribological performance. Tribology of FRPCs is quite complex than metal tribology due to the fact that polymers do not obey the well-established laws of friction at high temperature [37]. Xue and Wang [38] studied the effect of filler particle size on the wear and frictional properties of polymer composites. The authors concluded that addition of nano-sized SiC particles into the polymer matrix effectively reduced the friction and wear of the neat polymer. The nano-sized particles form a continuous and thin layer between the interface, which results in reduction of friction and wear. Xing and Li [39] also confirmed a similar behavior of FRPCs with the incorporation of nano-sized fillers. Gears, bearings, shoe soles, and brake pads for automobile applications are some of the mostly used tribological applications of FRPCs [40–42]. Researchers have suggested a number of methods to reduce the friction and wear at the interface between the FRPC product and the metal/nonmetal surface. Microencapsulation of liquid lubricant was found to be an effective method to improve the tribological properties of polymers [43]. Guo et al. [44, 45] demonstrated that the friction coefficient of epoxy-based FRPCs can be reduced up to 75% by incorporating just 10 wt% oil-loaded microcapsules. The authors have claimed to develop self-lubricating polymer-based materials with the help of encapsulation method. Khun et al. [46] and Imani et al. [47] added wax-loaded microcapsules in epoxy matrix composites and found that friction and wear were very much reduced in comparison to that in the neat epoxy polymer composite. In another study, Khun et al. [48] used the two types of microcapsules in the polymer composite. One type of microcapsules were loaded with wax and another type of capsules were loaded with MWCNTs. The authors concluded that tribological and mechanical properties were enhanced simultaneously. Wax-loaded capsules were found to be responsible for improved tribological properties while MWCNTs loaded capsules result in improved mechanical properties, which was achievable with only wax-loaded capsules. Encapsulation may help in the development of self-healing materials as explained by some authors [49].

Self-reinforced composites (SRCs) are yet another category of FRPCs in which only a single polymer is used. Hard/processed form of the same polymer is used as reinforcement that is being used as matrix material [50]. Huang [51] developed a polypropylene (PP)-based SRC using melt-flow induced crystallization. Li and Yao [52] and Makela et al. [53] developed PLA polymer-based fibers that could be used as reinforcement in the SRCs. Similarly, Tormala [54] developed PLA-based SRCs for medical applications. In the same series, Hine and Ward [55] developed PET-based SRCs, Gilbert et al. [56] developed polymethyl methacrylate (PMMA)-based SRCs, and Gindl and Keckes [57] manufactured cellulose-based SRCs.

Gemi [58] developed glass and carbon-based hybrid composite pipes and studied the effect of stacking sequence. The authors concluded that glass–carbon–glass sequence of reinforcement during the winding of fibers leads to no leakage property of pipes.

The superior electrical, mechanical, and thermal properties of graphene make it very useful in the field of FRPCs [59]. Graphene, in the form of 3D foam and gel is being used in FRPCs products in biomedical and electronics applications [60, 61]. Various authors [62, 63] reported impressive improvement in the mechanical properties of epoxy composites with the incorporation of 3D foam. Sun et al. [64] reported that the incorporation of 3D graphene foam in polymer significantly improved electrical properties. Jusza et al. [65] developed luminescent composite materials for possible applications in opto-electronics, sensor networks, and imaging field. Complex technology and expensive manufacturing methods of optically active two-phase composite materials have made them commercially unavailable.

Carbon nanotubes, popularly known as CNTs, are filler/reinforcement that are being used in polymers to fabricate composites with improved physical, mechanical, and electrical properties [66–69]. Nanomaterials are those materials that have dimensions below 100 nm [70]. Several authors [71, 72] reported an increment of over 300% in the tensile strength of FRPCs reinforced with CNT-based nano-fillers. Incorporation of nanocarbons resulted in the increment of electrical properties up to over 14 orders of magnitude [73]. Carbon quantum dots (CQD), a form of nanocarbon material, is also being used as reinforcement due to their tunable optical and photochemical properties. Another emerging class of FRPCs is thermally conductive polymer composites and nanocomposites [74]. Studies [75, 76] have reported that polymers reinforced with aligned molecular chain can obtain higher thermal conductivity than that of many metals. Rajapakse et al. [77] prepared electronically conductive nanocomposites for potential application as a cathode material.

Another advancement in the field of FRPCs is the production of shape memory polymer composites along with self-healing properties [78]. FRPCs are being widely used in the field of electronics and biomedical and energy applications from the last decades. However, low thermal conductivity and insufficient thermal stability have restricted FRPCs usage to a limited number of applications [79].

Along with their advantages, there are some disadvantages associated with FRPCs as well. The disadvantage with FRPCs is the need for recycling and disposal methods after the finite life of the FRPC product. Li et al. [80] investigated the environmental and financial problems associated with the manufacturing of carbon FRPCs. The authors suggested the use of mechanical recycling of FRPCs instead of landfilling and incineration. Landfilling method for disposal of FRPCs was found to be modest with moderate landfilling tax. However, incineration method results in the production of greenhouse gases causing severe damage to environment. Longana et al. [81] suggested another method of recycling known as multiple closed loop recycling of carbon FRPCs. In this method, reclaimed carbon fibers (rCF) are again used to remanufacture a number of products once a virgin carbon fiber (vCF) product has completed its defined life.

1.3 FRPCs Applications and Future Prospects

The high strength to weight ratio of FRPCs makes them irreplaceable in a number of applications in the automobile and aerospace industries [82–86]. Dhruv, the advanced light helicopter (ALH) manufactured by Hindustan Aeronautics Limited for the service of the Indian army, has around 60% of structural area made up of FRPC components and sandwich structures [87]. A number of products are being successfully used in various automotive and other applications as reported in Table 1.3. A number of medical devices have been developed using biodegradable polymers alone. Drug-eluting stents, orthotropic devices, disposable medical devices, drug delivery devices, and stents for urological applications are some biomedical applications of polymers [101]. Tian et al. [101] stated that along with the nontoxic nature and low biodegradability of polymers, mechanical strength is also required in a number of medical applications. To strengthen these biodegradable polymers, fibers are being incorporated in the polymers according to the requirement of application. Carbon fiber reinforced epoxy composite materials are being used to fabricate external fixation equipment used for fractured bones. Bone plates are being used for the development of internal fixation equipment. The authors [102] have reported carbon fiber reinforced polyether ether ketone (PEEK)-based composite as a biocompatible material for bone plate. Lin et al. [103] proposed short glass fiber reinforced PEEK composite material for the fabrication of intramedullary nails, which are generally used to fix fractures of long bones. These nails are fixed in the intramedullary cavity using a screw mechanism. Kettunen et al. [104] used carbon fiber to fabricate composite material for these nails. Some authors [105, 106] have successfully used FRPCs as bone grafting materials. Carbon fiber-based FRPCs are intensively being used to fabricate stems for total hip replacement [107, 108]. Deng and shalaby [109] used ultrahigh molecular weight polyethylene (UHMWPE) to fabricate self-reinforced composite materials for possible application in knee replacement. In dental applications, CF/epoxy-based FRPCs are being used to fabricate dental post [110]. Usually, gold bridges were used to replace one or more teeth but their high cost and time-consuming fabrication process have led to the development of FRPCs-based bridges [111]. FRPCs are also being used to fabricate orthodontic arch-wires. These wires are generally fitted over the teeth in order to align them [112, 113]. Artificial legs, used to support amputees during walk, were generally made of metallic materials. Owing to the high weight of metals and low corrosion resistance, FRPCs have replaced these metallic prosthetic limbs. As of now, all the three components of prosthetic leg, namely shaft, socket, and foot, are being manufactured using FRPCs [114–116]. Moving tables, used in CT and MRI scanners, are being manufactured using FRPCs due to the requirement of lightweight and high strength material [117]. Calcium phosphate (CaP)/polymer composite materials are highly recommended materials in bone replacement due to high compressive and flexural strength [118].

Table 1.3 Applications of reinforced polymer composites.

S. No.	Composite	Processing technique	Application field	Component	References
1.	Glass fiber/unsaturated polyester	Hand lay-up method	Automobile	Front bumper	[88]
2.	Sisal, roselle fiber, banana/epoxy grade 3554 A	Hand lay-up method	Automobile	Visor in two-wheeler	[89]
				Indicator cover	
				Pillion seat cover	
				Rear view mirror cover	
3.	Glass, carbon fiber/epoxy	—	Aerospace	Vertical stabilizer	[89]
4.	GFRPC/epoxy/polyester/pp	—	Electronic	Computer, electric motor covers cell phones	[90]
			Home and furniture	Roof sheet, sun shade, book racks, etc.	
			Aerospace	Luggage rack, bulkheads, ducting, etc.	
			Boats and marine	Boat frame	
			Medical	X-ray beds	
			Automobile	Body panel, seat cover, bumper, and engine cover	
5.	CFRP laminates	Vacuum bagging	Aerospace	Upper deck floor berns	[91]
				Pressure bulkhead	
				Centre wing box,	
				fin box, rudder HTP box	
6.	Glass, carbon, aramid/polyester, vinyl ester, epoxy	Filament winding, resin infusion, prepreg, etc.	Energy industries	Wind turbine blades	[92]

7.	CFRP	—	Automobile	Citroen car body	[93]
8.	CF-GF/epoxy (hybrid)	—	Aerospace	Pilot's cabin door	[94]
	Boron–graphite (hybrid)	—		Fighter aircraft components	
	CF–aramid/thermoplastic hybrid	—	Safety	Helmet	
	GFPR, CFPR (hybrid)	—	Civil	Bridge girder	
9.	CF/epoxy	Extrusion, compression molding	Automobile	Stiffener, floor panel, side sill inner	[95]
10.	CFRP	—	Automobile	Door sill stiffeners	[96]
				Engine bay subframe	
11.	CFRP/vinyl ester	Compression molding	Automobile	Fender support, headlamp supports, door components	[97]
	GFRP/vinyl ester			Door inner panel, windshield surround outer and inner panel, door components	
12.	CF/Epoxy	—	Biomedical	Prosthetic limbs (foot)	[98]
13.	Kevlar/CF/PMMA	—	Biomedical	Bone cement (used for fixing the bones)	[99]
14.	E-glass/epoxy	Pultrusion	Electrical applications	Insulating material for high voltage line	[100]

1.4 Conclusion

RPCs are engineered materials used in a wide spectrum of applications ranging from domestic products to biomedical devices. Natural and synthetic fibers are both being reinforced in FRPCs according to the application. FRPCs offer a number of advantages over conventional monolithic materials such as corrosion resistance, light weight and high strength to weight ratio. Automobiles, aircrafts, boats, ships, recreational goods, chemical equipment, and civil building and bridges are some common applications of FRPCs. Biomedical applications such as prosthetic legs and bone cement are relatively new applications of FRPCs-based materials. The consumption of FRPCs in the near future is expected to increase but a lot research is needed in the recycling and disposal methods of synthetic FRPCs.

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