Structural/Load-Bearing Characteristics of Polymer–Carbon Composites



Madhab Bera, Pragya Gupta and Pradip K. Maji

Abstract In the last few years carbon-containing polymer composites have drawn significant attention due to their light weight, high thermal stability, excellent mechanical, and electrical property. Important characteristics of carbon-based materials (CBMs) like high specific surface area and high strength have made them as very good reinforcing filler for a wide range of polymers. The foremost aspiration of this chapter is to establish a relationship between the structures and load-bearing performance of carbon-containing polymer composites. Structural diversities of CBMs such as carbon black, carbon fiber, carbon nanofiber, diamond, nanodiamond, graphite, carbon nanotubes (CNTs), and graphene are reflected in the differential load-bearing characteristics of their polymer composites. The chapter also provides state-of-the-art information regarding the potential applications of polymer/carbon composites.

Keywords Graphene \cdot Carbon nanotubes (CNTs) \cdot Fullerene \cdot Graphite Carbon fiber \cdot Load-bearing characteristics

1 Introduction

Carbon is one of the most important and versatile elements of the periodic table. It served the most to the mankind compared to any other elements. Sometimes, it spellbound the mankind as sparkling diamond and sometime it serves as fuel. It is

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almost impossible to imagine life in this planet without carbon, because most of the living organisms are made out of it. The most interesting feature of this material is its ability to assume variety of forms by simple carbon–carbon linking. It can exist in the form of diamond which is the strongest material in the world. It can also exist in the form of graphite which is soft in nature. Other forms of carbon like fullerene, carbon nanotubes (CNTs), graphene, carbon black, carbon fibers, and carbon nanofibers are unveiling day by day. Although, the carbon-based materials (CBMs) are structurally and property wise different from one another but one similarity exists among them and that is they are all made out of carbon only. Hybridization state of all these CBMs changes from sp² to sp³ as shown in Fig. 1.

They have extraordinary physical and chemical properties like high strength, excellent thermal and electrical conductivity, good corrosion resistance and extraordinary thermal and mechanical stability. This uniqueness has drawn a great attention to the researchers and scientists working all over the world. They are working hard to make innovative products by utilizing these CBMs. Nowadays, the use of CBMs is ubiquitous. They are being used in biological field, medicines and energy storage, structural composite parts, etc.

Polymers are an indispensible part of carbon-containing polymer composites and are usually of high molecular weight materials. They have low modulus and strength. The deformability of complex structures and sliding of polymer chains over one another makes them weak. Various reinforcing fillers like clay, silica, CaCO₃ can be used to improve the load-bearing characteristics (ability to carry load) of polymers. One of the most important additions in the filler category is carbon-based materials. Although, research on carbon-based polymer composites is going from many decades but a major breakthrough in this field occurred after the auspicious discovery of CNTs in 1991 by Japanese physicist Iijima [1] and graphene by A. K. Geim and K. S. Novoselov from Manchester University in 2004 [2]. Thousands of research papers in SCI/Scopus database (between 2013 and 2018) with the keywords "carbon nanotubes (CNTs)" and "graphene" proves it. Surface chemistry of CBMs plays a significant role in determining the physical and chemical properties of carbon-based materials and is greatly influenced by the presence of heteroatoms like oxygen, nitrogen, sulfur, phosphorus, boron, etc. For example, the electrical conductivity of graphene and carbon nanotubes increases many fold with the incorporation of nitrogen, sulfur, or phosphorus heteroatoms in the structures. Incorporation of oxygen makes CBMs polar and become compatible with polar organic polymers. Unlike other traditional fillers like glass fiber, talc,



Fig. 1 Hybridization states of different carbon-based materials

calcium carbonate, etc., most of the CBMs are of light weight and has high specific surface area; hence, they can be used as efficient reinforcing material for a variety of polymers, starting from thermoplastic to thermoset, rubber to elastomer. A small amount of filler loading provides maximum reinforcement in the polymer matrix, resulting light weight composite materials. In this chapter, we have elucidated the effect of structure of CBMs and polymers on the load-bearing characteristics of the nanocomposites and also their important applications in solar cells [3–7], battery [8], supercapacitors [9], water purification membrane, automotive body parts [10, 11], packaging, infrastructure [12, 13], biomedical applications [14–22], electronics, etc. Factors related to load-bearing characteristics of a composite material are also important part of this chapter.

Overall, it gives state-of-the-art information regarding the load-bearing characteristics of carbon-containing polymer composites and their potential applications in various emerging areas.

2 Carbon-Based Materials

2.1 Classification of Carbon-Based Materials

Carbon atoms can link together in a variety of ways to produce structures having completely different properties and thus forms the allotropes. Based on the structure and properties, carbon-based materials can be classified into the following categories (Scheme 1).

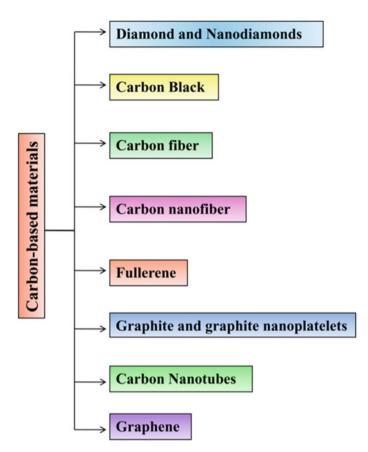
Out of these eight categories carbon nanotube (CNT) and graphene are the two most emerging CBMs having maximum scientific curiosity in the recent time.

2.2 Structure of Carbon-Based Materials

Structure of different carbon allotrope is very important in the load-bearing characteristic of the composites. Concise information regarding every CBM has been discussed as follows.

2.2.1 Graphene

Graphene is one of the most important carbon-based nanomaterials which is recently at the center of scientific curiosity. The two-dimensional (2D) nanomaterial has hexagonal close pack structure where every carbon atom is sp² hybridized and arranged in a honeycomb crystal lattice [23]. Graphene is nothing but the single layer of multilayer material, graphite. Thickness of graphene layer is around



Scheme 1 Classification of carbon-based materials

0.30 nm. Due to the presence of long range π -conjugation, it has outstanding physical properties. It is one of the strongest materials in the world with Young's modulus of 1 TPa and tensile strength of 130 GPa [24]. It has exceptionally high thermal and electrical conductivity also. Thermal conductivity of graphene is as high as 5000 W m⁻¹ K⁻¹ [25] and electrical conductivity can be more than 200,000 cm² V⁻¹ S⁻¹ in suspended graphene [25]. Due to very high specific surface area (~2630 m²/g) and high aspect ratio the material has an inherent tendency to agglomeration. Hence, dispersion of this material to a variety of polymers is a big challenge for the researchers. This limitation can be overcome by functionalization of the material with some polar groups so that the agglomeration tendency is reduced and the material become compatible with polymer matrix. In this context, reduced graphene oxide (RGO) comes into the field which is almost similar to pristine graphene in terms of structure and properties and has better compatibility with a range of polymers due to presence of very less number of oxygen containing functional groups.

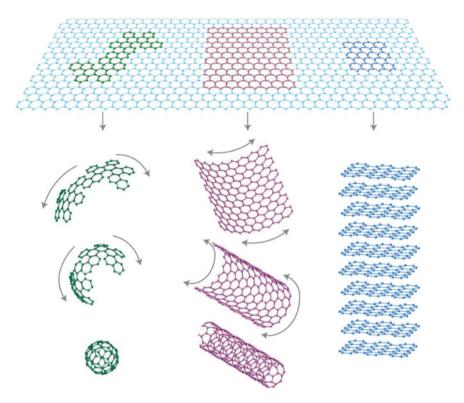
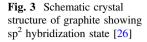


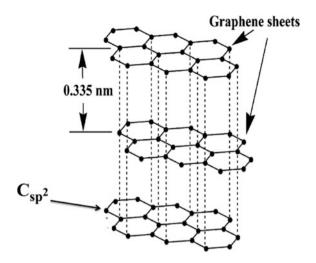
Fig. 2 Graphene (top) is the 2D building block of other carbon-based materials of all other dimensions. It can be wrapped up into 0D buckyballs (bottom left), rolled into 1D nanotubes (bottom middle) or stacked into 3D graphite (bottom right). Reproduced with permission from Ref. [23]. Copyright 2007, Springer Nature

Graphene is the building block of other carbon nanomaterials in other dimensions. It can be rolled-up to make 1D CNTs, wrapped to make 0D buckyballs and stacked together to make 3D graphite (Fig. 2).

2.2.2 Graphite and Graphite Nanoplatelets

Graphite is 3D soft and crystalline allotrope of carbon. It is formed by stacking more than 100 number of atomically thick carbon layers. In graphite structure, every carbon atom is sp^2 hybridized and covalently bonded with three other carbon atoms to forms hexagonal close pack structure. Although, the covalent bonding among the carbon atoms of individual layers are very strong but the bonding among the layers are very weak (Van der Waals forces). The layers can slide over one another and makes it a softer material compared to diamond [26]. The interlayer distance in graphite is 0.34 nm (Fig. 3). Inherent electrical conductivity is one of





the most important properties of graphite that has been used in different speciality applications.

Graphite nanoplatelets have similar structure to that of graphite, only the inter-planer distance is greater than graphite. Its thickness is ~ 10 nm and size ranging from sub-micron to 15 µm or even greater. From the economic point of view, this material is very less expensive than most other carbon-based materials. It is 100 times cheaper than CNTs and has very good mechanical and electrical properties [27]. This material can be used to make polymer nanocomposites that are economically viable.

2.2.3 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are one-dimensional (1D) crystalline allotropic form of carbon having diameter in nanometer scale and length of several micrometers. They have hollow cylindrical structure with wall made up with atomically thick 2D (graphene) material [28]. Based on the number of layers in the wall, CNTs can be classified into single walled carbon nanotube (SWNTs) and multiwalled carbon nanotubes (MWNTs) [29] (Fig. 4). The structure of SWNTs can be imagined to form by rolling up a single sheet of graphene into a cylindrical shape. Chirality of nanotubes is dependent on the way graphene sheet is rolled and represented by a pair of miller indices (*n*, *m*). The roll up vector is represented as $C_h = n\bar{a}_1 + m\bar{a}_2$. Here, the integer "*n*" and "*m*" denotes the number of unit vectors (*a*₁, *a*₂) along two directions of graphene crystal lattice. Depending on the values of "*n*" and "*m*" there exist three different configurations of CNTs. If *m* = 0, the nanotubes. In all other cases ($n \neq m$) the nanotubes are called **chiral** nanotubes (Fig. 5) and its chiral angle (θ) is within 0°–30° [30]. Single-walled carbon nanotubes are an important

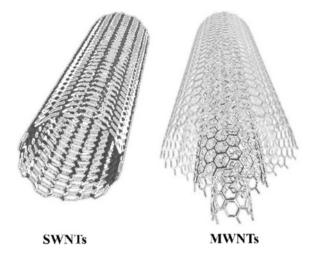


Fig. 4 Schematic diagram of single wall carbon nanotube (SWNTs) and multi wall carbon nanotubes (MWNTs) [29]

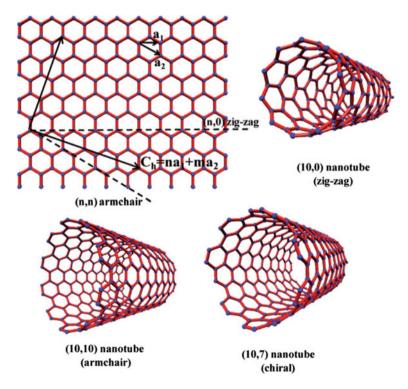


Fig. 5 A graphene sheet is rolled to show the formation of different types of SWNTs. Reproduced with permission from Ref. [30]. Copyright 2009, Royal Society of Chemistry

member of carbon filler family because their properties changes significantly with (n, m). Diameter (d) of the nanotubes can be calculated from the Eq. (1) by using the n and m value and chiral angle can be calculated from Eq. (2)

$$d = \frac{a}{\pi}\sqrt{(n^2 + nm + m^2)} \tag{1}$$

$$\cos\theta = \frac{(2n+m)}{2\sqrt{(n^2+nm+m^2)}}\tag{2}$$

The diameter of SWNTs is ~ 1 nm where the same for MWNTs are 5–50 nm. SWNTs provide better reinforcing effect compared to MWNTs at the similar loading due to high specific surface area [30].

In case of multiwalled carbon nanotubes, the number of graphene layer in the wall is more than two and the interlayer distance between the layers is same as it found in graphite (0.34 nm). In MWNTs individual layers are held together by van der Waal forces or more specifically π - π stacking. Due to extended conjugated structure, CNTs have extraordinary thermal and electrical conductivity and very good mechanical properties.

2.2.4 Fullerene

Fullerenes are the third allotropic form of carbon after graphite and diamond and have a variety of shapes [31]. The zero dimensional (0D) nanomaterials may exist in the form of hollow sphere, ellipsoid and many other shapes. Spherical fullerene, similar to the shape of a football, containing 60 carbon atoms or buckminster fullerene (C_{60}) is the most popular among the scientists and researchers. It is so popular that when we are talking about fullerene we mean to say about C_{60} . Although, other forms of fullerenes like C₂₀, C₅₀, C₂₄, C₇₀, etc., are also exist (Fig. 6). Structure of fullerene is quite similar to that of graphite, i.e., stacking of several layers of hexagonal graphene sheets. Fullerenes may have pentagonal or heptagonal rings in their structure. Every carbon atom in fullerene is sp^2 hybridized. The hexagonal graphene sheet is bent to form a closed sphere. This kind of bending introduces angular strain within the structure making fullerene highly reactive and susceptible for organic modification. Solubility of fullerenes is an important criterion for making polymer/fullerene composite by solution casting method [31]. Most of the fullerenes are insoluble or sparingly soluble in most of the solvents. However, only C₆₀ is easily soluble in toluene and carbon disulfide at room temperature.

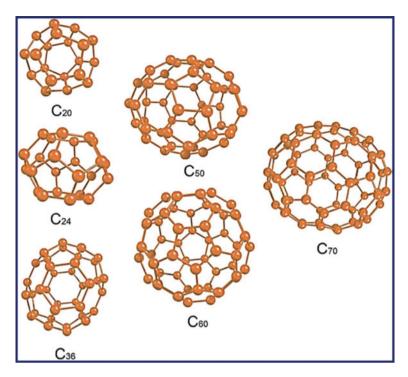


Fig. 6 Schematic structure of fullerene molecules [31]

2.2.5 Diamond

Diamond is extremely hard, transparent, and crystalline allotrope of carbon having tetrahedral structure. All the carbon atoms in diamond are sp³ hybridized and strongly bonded (σ bonding) with neighboring carbon atoms forming a giant-like tetrahedral structure (Fig. 7). This kind of giant like structure makes it the toughest and strongest inert solid with high thermal conductivity and optical transparency. Since, the entire valence electros are used up for forming covalent bonds, there is no free electrons to conduct electricity. Diamond is electrically insulator. Silicon, Germanium and Gallium has similar kind of crystal structure.

2.2.6 Nanodiamond

Structure of nanodiamond is little bit complicated consisting of three layers; (i) the diamond core is made up with sp^3 hybridized carbon atoms; (ii) fullerene like shell of sp^2 hybridized carbon atoms partially covers the core and (iii) the outer layer consists of carbon atoms which forms functional groups by terminating with hydrogen and oxygen atoms (Fig. 8a). Various functional groups are identified on

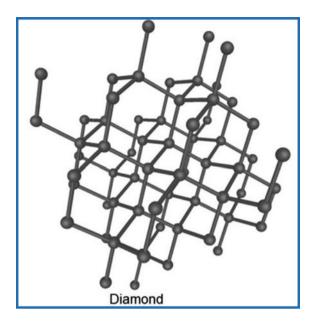


Fig. 7 Schematic crystal structure of diamond [32]

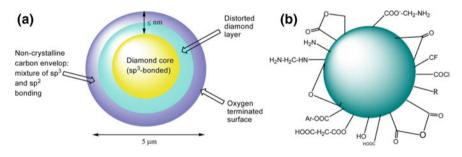


Fig. 8 a Model of nanodiamond structure; b schematic representation of various functional groups present on nanodiamond surface [33]

ND surface. They may be hydrocarbons like $-CH_3$, $-CH_2$ and -CH in different configurations or oxygen containing functional groups like ether (-C-O-C-), carboxylic acid (-COOH), carbonyl (-C=O) and lactone (-O-C=O), etc. (Fig. 8b). On the basis of particle size, nanodiamond particles are classified into three categories, (i) nanocrystalline particles (ii) ultra-nanocrystalline particles and (iii) diamondiods. Size of nanocrystalline particles are in the range of tens of micrometer while the same for ultra-nanocrystalline particles are within several nanometers and for diamondiods particles it normally lies within 1–2 nm. Average size of ND particles is 2–8 nm. Although, the size may be varied up to 20–25 nm depending on the process variables like weight of the explosive charge [32]. Nanodiamonds are non toxic. They have excellent mechanical properties, high surface area,

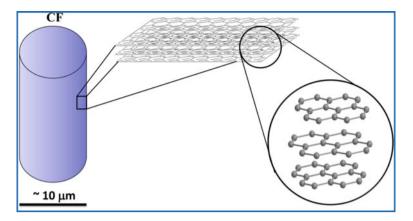


Fig. 9 Cross section of carbon fiber showing the microstructure

hardness, chemical stability and tunable surface chemistry and hence they can be used in microelectronic devices, super hard coating, antifriction coating, biomedical applications, etc.

2.2.7 Carbon Fiber (CFs)

Carbon fiber is an important member of carbon family. It is a fiber like non-crystalline material with diameter 5–10 μ m and consists of mostly carbon atoms (Fig. 9). The material contains around 92% carbon where every carbon is sp² hybridized and strongly bonded with one another. This kind of strong inter-carbon bonding provides carbon fiber excellent mechanical property and chemical stability. It has very high tensile strength (2–7 GPa), tensile modulus (200–900 GPa), and low density (1.75–2.20 g/cm³). Carbon fiber has also excellent thermal and electrical conductivity but has low thermal expansion coefficient. One interesting observation about carbon fiber is that although it is four times lighter than steel but it is many times stronger. This is the prime advantage of carbon fiber to develop light weight composite materials for structural applications [34, 35].

2.2.8 Carbon Nanofiber (CNFs)

Carbon nanofiber (CNFs) or vapor-grown carbon nanofiber (VGCNFs) are one-dimensional nanomaterials with cylindrical structure. In CNFs structure graphene layers are stacked together in different arrangements like cone, plate, or cup. Typical diameter for VGCNF is 50–200 nm and length can be up to 100 μ m. Because of very high aspect ratio (250–2000) CNFs can act as efficient reinforcing filler for a wide range of polymers [35]. CNFs are usually synthesized by catalytic chemical vapor deposition (CCVD) or simply chemical vapor deposition

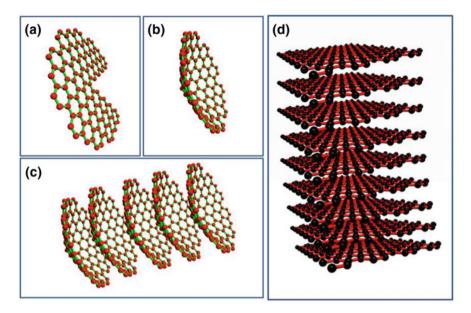


Fig. 10 Schematic representation of cup-stacked CNF structure **a**–**c**; and **d** platelet CNF structure. [36]

(CVD) and electro spinning method. Two types of CNFs are synthesized by CCVD method: cup-stacked CNF and the platelet CNF (Fig. 10). CNFs produced by electro-spinning method have a tendency to form web or mat like structure. This type of materials is specially recommended for batteries and/or supercapacitors applications [36].

There are certain basic differences between carbon fibers (CFs) and carbon nanofibers (CNFs): one important difference is obviously the diameter. CFs have diameter of several micrometer whereas the diameters of CNFs are 50–200 nm only. So, CNFs acts as better reinforcing filler compared to CFs due to its high surface area. The structure and preparation method of the two materials are quite different. These two materials are widely used in energy storage device and reinforced composites.

2.2.9 Carbon Black

Carbon black is a colloidal form of elemental carbon, synthesized by incomplete combustion of oils or natural gases. Carbon black particles are normally spherical in shape with particle size ranging from 10 nm to 500 nm. Particle size of carbon black is determined by Iodine (I_2) adsorption test [37] and surface area is determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption test. Due to very high specific surface area and surface energy, carbon black particles have a natural

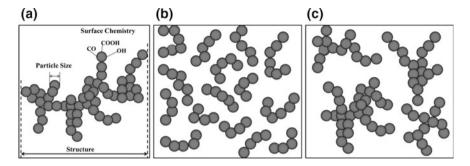


Fig. 11 a Schematic representation of particle size, structure and surface chemistry of carbon black, b low structure carbon black c high structure carbon black

tendency to fuse together and form aggregates. These are called the structure of carbon black (Fig. 11a). There are two types of structures for carbon black, low structure (Fig. 11b) and high structure (Fig. 11c). When large number of individual carbon black particles are fused together to form a long and branched chain (grape-like structure), it is called high structure. This kind of carbon black is perfect for reinforcement of compounds, where desired conductivity can be achieved at very lower loading. In case of low structure, small number of individual carbon black particles are fused together to form short and linear structures [38, 39]. Structure of carbon black is determined by dibutyl phthalate (DBP) absorption test and expressed as number of cm^3 of DBP absorbed by 100 g of carbon black. Normally, increase in structure size leads to an increase in dispersibility of the particles but decreases the blackness. Other properties related to carbon black structure are shown in Table 1. The blackness is also related to particle size of the carbon black. Smaller the particle size, greater is the darkness/tinting strength of carbon black but poor dispersibility. This is due to strong cohesive forces among the carbon black particles. Based on the abrasion resistance, extrusion rate, manufacturing process, structure and surface area, ASTM D1765 [40] has classified carbon blacks into certain categories as shown in Table 2.

Property	High structure	Low structure
Dispersibility	Easier	More difficult
Adsorption	Low	High
Wetting	Slower	Faster
Gloss	Lower	Higher
Conductivity	Higher	Lower
Viscosity	Higher	Lower
Loading capacity	Lower	Higher
Tint strength	Lower	Higher

Table 1 Effect of structureon compound properties [39]

• •				
Name	Standard abbreviation	ASTM designation	Particle size (nm)	Avg. N_2 surface area (m ² /g)
Super abrasion furnace	SAF	N110	15–18	124–130
Intermediate SAF	ISAF	N220	20–25	112–115
High abrasion furnace	HAF	N330	28–36	76–80
Fast extrusion furnace	FEF	N550	39–55	39–41
General purpose furnace	GPF	N660	56–70	34–36
Semi reinforcing furnace	SRF	N770	71–96	31–32
Fine thermal	FT	N880	180-200	17–20
Medium thermal	MT	N990	250-350	7–9

Table 2 Typical rubber grade carbon blacks with their particle size and surface area [40]

In Table 2, the letter "*N*" indicates the normal rate of curing. In some cases the alphabet "*S*" is used which indicates slow curing rate. The first numeral, immediately after the alphabet indicates the particle size range which increases with the increase in number. The remaining two numerals are selected arbitrarily. In case of carbon black with standard level of structure, the second numeral is always the repeat of first numeral and the third numeral is kept as zero [39].

2.3 Comparison of Physical and Mechanical Properties of CBMs

The versatile material, carbon can exists in different allotropic forms having different crystal structures. Due to the structural diversity of CBMs, their physical and mechanical properties become distinctly different. The physical and mechanical properties of all the CBMs are summarized in Table 3 for better clarity and understanding.

3 Properties Related to Load-Bearing Characteristics of Carbon-Containing Polymer Composites

In order to understand the load-bearing characteristics of carbon-containing polymer composites, it is almost essential to have an elementary insight regarding the basic properties that are related to load-bearing characteristics. Strength, modulus of

important a second		arting to controlotid mate full and material articleting of the						
Carbon-based	Morphology	Diameter ^d /	Density	Aspect ratio	Specific surface	Tensile	Modulus	Reference
materials		thickness ^t (nm)	(g/cm^3)	(L/D)	area (m ² /g)	strength	(TPa)	No.
Nanodiamond	Particles: 3D	2–8 ^d					:	[33]
Carbon black	Particles: 3D	10–500 ^d			10–250	8– 25.2 MPa		[39, 40]
Carbon fiber	Rod: 2D	5000-10,000 ^d	1.75-2.2	440		2–7 GPa	0.2-0.90	[74, 75]
Carbon nanofiber	Cylindrical: 1D	50-200	2	250-2000		2.92 GPa	0.24	[75]
Fullerene	Dot: 0D	0.4–1.20 ^d	:	:		:		[59]
Graphite	Ellipsoid: 3D	2000–200,000	2.26			130 GPa	1	[29]
Graphite nanoplatelets	Ellipsoid: 2D	10 ^t					:	[27]
SWNTs	Needles: 1D	0.5–2 ^d	0.80	100-10,000	40	50–500 GPa	~1	[29, 75]
MWNTs	Needles: 1D 5–50 ^d	5-50 ^d	1.80	100-10000		10–60 GPa	~ 0.3 –1.0	[29, 75]
Graphene	Flakes: 2D	0.30^{t}	:	:	2630	130 GPa	1	[2]

Table 3 Important mechanical and physical properties of CBMs

elasticity, stiffness, hardness, toughness, ductility, fatigue, creep, temperature resistance and corrosion resistance are the most important properties for load-bearing capacity of the composite.

3.1 Strength

Strength is the ability of a material to withstand load without being failure or plastic deformation. Strength may be of three types: **tensile strength**, **compressive strength** or compression strength and **flexural strength**. Amount of stress required for complete failure of a material is called its ultimate tensile strength (UTS) or tensile strength. It is remarkably different from the modulus of a material. Flexural strength is defined as the stress at failure in bending test. It is normally measured by three point bending test. Compressive strength or compression strength is the ability of a material or structure to withstand the load against compression. So, compression strength and tensile strength are just opposite to each other. The former withstand load which tends to reduce the size whereas the later withstands loads which tends to elongate the material. Strength of a carbon-containing composite material primarily dependent on the strength of the CBM used in composite and the strength of the polymer matrix. For polymer composites the term tensile strength has the maximum use.

3.2 Modulus of Elasticity

Modulus of elasticity or elastic modulus is defined as a measure of resistance of a material or an object against elastic deformation. It is normally expressed as stress/ strain in the elastic region of stress versus strain curve (Eq. 3).

Elastic modulus (E) =
$$\frac{\text{Stress}}{\text{Strain}} = \frac{(\text{Force/Area})}{(\text{Increased length/Initial length})} = \frac{(F/A)}{(l/L)},$$
 (3)

where, F is the applied force, A is the cross-sectional area of the test specimen; L is the gauge length of the specimen; l is the increased length.

3.3 Stiffness

Stiffness is the ability of a material to resists deformation when external force is applied. Stiffness is related to the structure of the material (Eq. 4).

Structural/Load-Bearing Characteristics of Polymer-Carbon ...

Stiffness
$$(k) = \frac{F}{l}$$
, (4)

where, F is the applied force and l is the change in length

So, a material having high elastic modulus is a stiff material.

3.4 Hardness

Hardness is an important mechanical property of a material used in coating, adhesives, hose pipes, etc. It is a measure of resistance of a material to plastic deformation. However, it can also be defined as the resistance to scratching, abrasion, or corrosion of a material. It is normally measured from the resistance of indention of an indenter. Durometer shore hardness is commonly used for polymers and its composites. It has two different scale **Shore A** and **Shore D**. Shore A is used for soft materials like rubber, elastomers, etc., and shore D scale is used for hard materials like cross-linked rubber and hard plastics. In both the scales, higher value indicates higher hardness of the material. The most well-known hard material is diamond and examples of soft materials are rubber, plastics, and their composites. Hardness is related to elastic modulus or stiffness of a material. Materials having high elastic modulus and stiffness will have high hardness.

3.5 Toughness

Toughness is the ability of a material to absorb energy and plastically deformed without being failure. So, in another term it is the absorbed energy per unit volume before failure. It is calculated by integrating a stress–strain curve (Eq. 5).

Toughness =
$$\frac{\text{Energy}}{\text{Volume}} = \int_{0}^{4} \sigma d\epsilon$$
 (5)

where,

 ϵ is strain

 ϵ_f is strain up to failure

 σ is stress

Normally, the total area under the stress–strain curve is the measure of toughness. Toughness of a composite material is important to make a balance between ductility and brittleness.

3.6 Ductility

Ductility is the ability of a solid material to be deformed under tensile loading. There is a direct correlation between ductility and toughness. Because ductile materials are normally tough and non-ductile materials are brittle. When a material is stretched up to the plastic deformation limit and then the stress is withdrawn suddenly. The stress–strain curve is not ended up with zero strain although stress value is zero. That means some strain still remains within the material and that is the origin of the material's ductility. If the stress–strain curve of a material is completely linear up to the breaking point (like hard steel) then the material has very little ductility. Materials having stress–strain curve with very long region after the yield point (like rubber, plastics, and polymer composites) are ductile.

3.7 Fatigue

It is the weakening of a material caused by cyclic loading. If a material is subjected to alternating stresses then the material will fail at much lower stress than the tensile strength of the original material. The reason behind such behavior may be due to the internal structural breakdown or molecular chain scission by cyclic loading which creates microcracks within the materials and hence fails at much lower stress.

3.8 Creep

Creep is defined as the time-dependent permanent deformation or plastic deformation of a material when the applied load remains constant. Creep does not occur immediately after the application of stress, it is a time dependent phenomenon. Creep value depends on the amount of stress applied, time duration and temperature. It is one of the major limitations of polymeric composite materials used in structural application. Creep value normally increases with increase in temperature.

3.9 Temperature Resistance

It is defined as the ability of a material to withstand higher temperature without getting decomposed or changed. Normally, temperature effect on a composite material by three ways: (i) Individual components present inside the composite material may react chemically in presence of high temperature. Although this effect is not so prominent for in situ synthesized polymer composites, (ii) the difference in thermal expansion coefficient between polymer and filler generates internal stress

and cracks, (iii) most materials exhibit creep behavior at high temperature. So, for higher load-bearing capacity, the composite material must have high temperature resistance.

3.10 Corrosion Resistance

Corrosion resistance of a material is its ability to withstand damage caused by temperature, chemicals or surrounding environment. Various cracks and scratches are on the composite surface because of corrosion which ultimately reduces the load-bearing capacity of the composite material. Hence, good corrosion resistance material has higher load-bearing capacity.

4 Load-Bearing Mechanisms of Carbon-Containing Polymer Composites

Mechanical properties like modulus, tensile strength, hardness, toughness, etc., of a composite material is related to its load-bearing efficiency. Normally, reinforcing fillers have greater modulus and tensile strength than polymer matrix [13]. Incorporation of reinforcing filler (CBMs) into the matrix leads to an increase in tensile strength and modulus. The question is how the load is being transferred. To get an explanation let us consider a simple fact that at a particular strain; filler carries more load than polymer. So, the load or stress is being transferred from matrix to the fillers via shear stress at filler/matrix interface and there is no stress at the end of the composite. The rate of load transfer is directly related to this interfacial shear stress [41]. Here, the structure of filler and the polymer plays an important role. Carbon-based materials have significantly different structures. Some are spherical or rod like, others are cylindrical- or flake-like structure. Their aspect ratio and mechanical properties are also different. They have different load-bearing capacity; but, the basic load-carrying mechanism is same for all cases. Thakur et al. [42] proposed a simple mechanism for the huge improvement in mechanical properties of hyper branched polyurethane (HPU)/functionalized reduced graphene oxide (f-RGO). According to their explanation toughness originates from the secondary bonds present between the polymer chains. At higher loading the secondary bonds ruptured and this allows to extend the long hidden polymer chains length, maintaining the structural integrity. The weak interlayer interaction between f-RGO sheets is also overcome by the applied load and the f-RGO sheets slide pass over one another, without damaging the original sheet like structure (Fig. 12).

During this process significant amount of energy is released. This increases the toughness of the material and the combine influence of polymer chain decoiling and

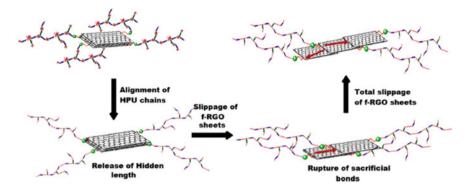


Fig. 12 Plausible Mechanism of High Elongation and Toughness of HPU/f-RGO Nanocomposites. Reproduced with permission from Ref. [42]. Copyright 2014, American Chemical Society

f-RGO sheets slipping increases the elongation at break of the composite materials. Due to the strong H-bonding interaction between f-RGO and polyurethane chains, the modulus and tensile strength of the composite materials increases.

5 Factors Influencing the Load-Bearing Characteristics of Carbon-Containing Polymer Composites

In any composite materials, load-bearing characteristics depends on a number of parameters: (i) nature of polymer and fillers (ii) dispersion of CBMs within the polymer matrix, (iii) loading of CBMs, (iv)interfacial interaction between polymer and CBMs, (v) notches and cracks on the materials and (vi) ambient conditions.

5.1 Nature of Polymer and Filler

Polymer composite consists of a continuous phase called polymer and a discontinuous phase or filler. Normally, fillers have better mechanical properties compared to that of polymers. In polymer composite most of the load is carried out by the fillers. For carbon-containing polymer composites CBMs acts as reinforcing filler and increases the load-bearing characteristics of the material. This can be proved from the basic equations of composites (Eqs. 6 and 7). Modulus of polymer composite in longitudinal direction

$$(E_{\rm c}) = (E_{\rm m}V_{\rm m} + E_{\rm f}V_{\rm f}) \tag{6}$$

The same in transverse direction
$$\frac{1}{E'_c} = \left(\frac{E_m}{V_m} + \frac{E_f}{V_f}\right),$$
 (7)

where, $E_{\rm m}$ and $E_{\rm f}$ are the modulus of polymer and filler respectively; $V_{\rm m}$ and $V_{\rm f}$ are the volume fraction of polymer and filler respectively; $E_{\rm c}$ and $E'_{\rm c}$ are the modulus of carbon-containing polymer nanocomposites in longitudinal and transverse direction respectively.

Table 3 illustrates the mechanical properties of different CBMs. From the basic equation of composite (Eqs. 6 and 7), it is clear that for different combinations of polymer and CBM, load-bearing characteristics will be different. For example, with the incorporation of 1 wt% of MWNTs to the polypropylene matrix, tensile strength increases by 20% and Young's modulus increases by 15%. In case of Nylon-6 under identical condition tensile strength increases by 120% and Young's modulus increases by 110% [43]. This is due to better mechanical properties of Nylon-6 over polypropylene.

5.2 Dispersion of CBMs

Homogeneous dispersion of CBMs into the polymer matrix is one of the most important criterions for designing high-performance composite materials. But, it is very difficult to disperse carbon-based nanofillers like graphene, CNTs, fullerene, carbon nanofibers, etc., within the polymer matrix. Because of very high specific surface area and high aspect ratio, the nanofillers have a natural tendency of aggregation. So, uniform dispersion of fillers is a great challenge to the material scientists and engineers. Non-uniform dispersion of filler leads to inferior load-bearing characteristics and hence poor mechanical properties of the composites [44]. Various studies suggest that three different kinds of morphological states (phase separated, intercalated, and exfoliated) exist in graphene, CNT, graphite nanoplatelets based polymer composites [45] based on the degree of filler dispersion (Fig. 13). Among these three morphological states exfoliated structure indicates the best filler dispersion, best load-bearing characteristics and hence best mechanical properties to the composites. The morphological differences can be observed through transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) instruments and reflected in the mechanical and other properties.

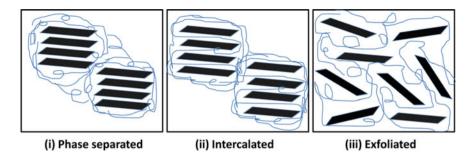


Fig. 13 Schematic representation of three different morphological states of graphene-polymer nanocomposites; a phase separated, b intercalated, c exfoliated [45]

5.3 Loading of CBMs

The concept of polymer composite was first come aiming to decrease the price of finished products by incorporating various kinds of low-cost fillers into the polymer matrix. But, with time it is found that filler not only reduce the price of final products but also increases the strength and load-bearing characteristics of the finished materials. It is quite obvious that increased filler loading leads to an increase in load-bearing characteristics of polymer composites but up to a certain limit; after which aggregation takes place causing a deterioration of the mechanical properties. For example, in case of PVDF/NDs composite tensile strength and Young's modulus increases with increase in NDs loading from 0 to 5% and at 5% loading, tensile strength increases by 105% and Young's modulus increases by

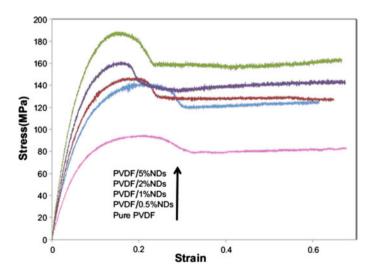


Fig. 14 stress-strain curve of PVDF/NDs composites at different loading of NDs [46]

110% [46]. The corresponding stress–strain curve is shown in Fig. 14. Similar type of improvement in mechanical properties is found with many other combinations of polymer/CBMs [47–49]. So, it is quite clear that the filler loading has an important role in the load-bearing capacity of carbon-containing polymer composites.

5.4 Interfacial Interaction Between Polymer and CBMs

Load-bearing characteristics of carbon-containing polymer composites depend to a great extent on the interfacial interaction between filler and polymer. For example, HIT and J-1 sizing agents are used to modify carbon fiber surface in order to improve the interfacial interaction between CFs and polymer as well as load-bearing capacity of the composite [50, 51]. Sizing agents are normally polymeric materials and are coated onto the carbon fiber surface during their manufacturing. Zhang et al. [52] studied the effect of sizing agent concentration on the mechanical properties of CFs and its composites at three different concentrations (1, 1.5, and 2 wt%) and found best results with 1.5 wt% loading of sizing agent. Ding et al. [53] also reported that interfacial interaction between polypropylene and carbon black increases with increase in the loading of silane coupling agent which was reflected from the improved mechanical properties of polypropylene/CB composites. Silane coupling agent was also used in HDPE/carbon black [54] and NR/carbon black composites [55]. Interfacial interaction between carbon black with CO₂.

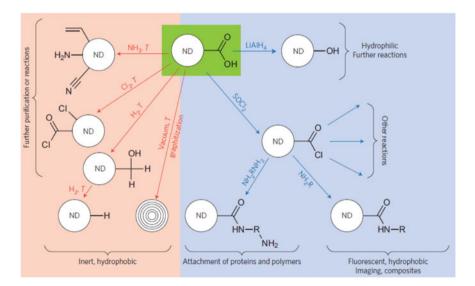


Fig. 15 Different types of surface modifications of NDs. Reproduced with permission from Ref. [57] Copyright 2011, Springer Nature

It develops surface heterogeneity of carbon black and hence increases the degree of adhesion between carbon black and SBR rubber [56]. In order to increase interfacial interactions, graphite is sometimes oxidized to synthesize graphite oxide which increases the interaction between polymer and filler. Kausar et al. [31] reported that the interfacial interaction between carbon fiber and epoxy resin increases with the addition of 2 wt% fullerene. Different type of surface modifications is also done to improve the interaction between NDs and polymers (Fig. 15). Similar to NDs, the surface of CNTs are also modified by attaching –NH₂, –COOH and –C=O functional groups to improve the interaction between CNTs and polymers [28].

5.5 Notches and Cracks

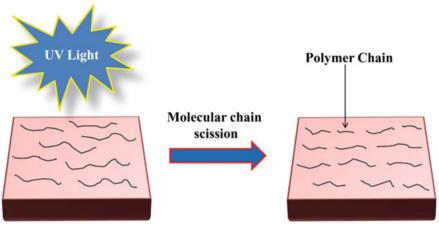
Microscopic cracks and notches generated in composite materials during processing, handling, transport, and service life also affect the load-bearing capacity of the composite materials. Cracks generated during service are mainly due to mechanical loading and long-term cyclic stress. Although, temperature, humidity, chemicals, UV radiation, and the presence of structural flaws also have some influence in crack generation. A detailed study about the formation, propagation, detection, and prevention of these notches and cracks are very important to monitor the load-bearing capacity. When energy required for crack growth is equal or larger than the energy required for the creation of a new surface, crack will propagate [58]. The reasons for crack generation are elaborated as follows.

5.5.1 UV Radiation

Upon long-term exposure of ultra-violet (UV) light, UV photons are absorbed by the polymer chains present in carbon-containing polymer composites and undergo photo-oxidation which leads to scission of polymer chains and/or cross-linking. Molecular chain scission generates polymer radicals and reduces the molecular weight (Fig. 16). Whereas, chain cross-linking makes the structure too much brittle, reduces the molecular mobility, and thus introduces microcracks within the composite structure. This kind of microcracks reduces the load-bearing capacity of the composite materials.

5.5.2 Thermal Effect

The thermal effect for crack generation it is very simple. Under extreme heating condition, there occurs a temperature gradient between the surface and the bulk of the composite material which introduces thermal stress to the material. This thermal



Polymer composite

Fig. 16 Effect of UV light on molecular chain scission on long-term exposure

stress is responsible for the initiation and growth of cracks. This type of cracking observed in carbon-epoxy composite [43].

5.5.3 Hydrothermal Aging

Carbon-based polymer composites are used in many structural applications like aerospace, automotive structure, building materials, etc. which are directly exposed to hydrothermal environments. Hydrothermal environment is an environment where combined effect of heat and moisture or humidity is present. Since many polymers absorb water or moisture they are getting swelled out of it. Also, by the capillary action of CBMs, it is easily transported to the fiber–matrix interface and reduces the interfacial bonding interaction. Under the combined influence of absorbed water and high temperature, some microcracks are generated at the interface which propagates with time. Thus, the load-bearing capacity of the composite will decrease.

5.5.4 Chemical Environment

Sometimes polymer nanocomposites are used in some harsh chemical environment. For example, the material used in marine structure always remains in highly salty ambient. In some other cases harsh acid or basic ambient also facilitate the generation of microcracks. Vinyl ester, epoxy and polyester resin based composites are normally used under such chemical environments.

5.6 Surrounding Environmental Condition

Environmental conditions also play a key role in the load-bearing capacity of carbon-containing polymer composites. Parameters related to ambient conditions are temperature, humidity, chemicals, and UV radiation. All these ambient conditions are also related to the generation of cracks and notches and have been discussed in the respective section elaborately.

6 Load-Bearing Behavior of Different Carbon-Containing Polymer Composites

6.1 Diamond and Nanodiamond/Polymer Composites

Since nanodiamond particles are very small (2–8 nm) they have very high surface area and surface energy and have a natural tendency of aggregation. Various modifications of NDs surface has been done to increase the compatibility between polymer and NDs. Jee et al. [59] reported that Young's modulus and hardness of LDPE/NDs composites enhance with increase in NDs loading and length of alkyl groups (Fig. 17). According to their observation, hardness increases by 4.5 times and Young's modulus increases by 2.5 times with the incorporation of 11 wt% ethylhexyl modified NDs. The structure and mechanical properties of NDs reinforced polymer composites have been investigated by other researchers also. Zhang et al. [60] have investigated the hardness and Young's modulus of ND/polyimide composites by nanoindentation method and found 15% increase in hardness and 30% increase in Young's modulus at 5 wt% loading of NDs. Behler et al. [61] have also measured the mechanical properties of ND/polyamide composites and

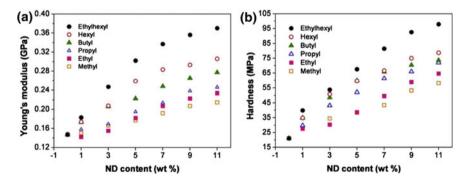


Fig. 17 Variation of **a** Young's modulus and **b** hardness of different alkyl chain functionalized NDs/LDPE composites as a function of NDs content. Reproduced with permission from Ref. [59] Copyright 2011, Elsevier

observed about two times increase in hardness and four times increase in Young's modulus with 20 wt% NDs. Neitzel et al. [62] reported 470% increase in Young's modulus and 300% increase in hardness of epoxy resin by adding 25 vol.% nanodiamond. Morimune et al. [63] synthesized poly- (vinyl alcohol) (PVA)/ND nanocomposites by solvent casting method and found 250% increase in Young's modulus and 40% increase in tensile strength of PVA with the addition of 1 wt% NDs.

6.2 Carbon Black/Polymer Composites

Carbon black is mostly used as a reinforcing filler to increase the mechanical, electrical and abrasion resistance property of polymers. About 90% of total carbon black manufactured worldwide is used in automotive tire industry to improve tear strength, modulus, and wear characteristics of the tires. The reinforcing nature of carbon black strongly depends on its surface area (type of carbon black) and their effect is reflected in the mechanical properties of their composite. Li et al. [64] observed that for ethylene-propylene-diene rubber(EPDM)/carbon black composite hardness, tensile strength, and modulus increases with increase in surface area of carbon black at 30 phr loading (Table 4). For SBR/carbon black (surface area = $80 \text{ m}^2/\text{g}$) composite tensile strength, tear strength and hardness increases by 895, 256, and 27% respectively with the addition of 20 phr carbon black after that the same decreases [65]. Natural rubber (NR)/carbon black composites are also used in the tire tread, sidewall to improve fuel efficiency (10%) and decreases rolling resistance (20%). Liang et al. [54] reported HDPE/silane coupling agent treated carbon black composites where mechanical properties like tensile strength, flexural strength, flexural modulus, and elongation at break increases up to 5 wt% loading of CB. Ao et al. [56] reported that mechanical property of N330 carbon black filled SBR rubber composite can be improved by using activated carbon black. According to the observation tensile strength and modulus increases up to 30 phr loading of carbon black. Shooli et al. [66] reported that tensile strength of 50:50 mixtures of SBR and epoxidized NR is increased by 158% with the addition of 35 phr carbon

Properties	N770	N550	N330	N472
BET surface area (m ² /g)	15.80	37.80	81.10	1039.50
Hardness (Shore A)	52	60	59	79
300% modulus (MPa)	2.91	5.17	5.23	15.12
Tensile strength (MPa)	12.12	15.04	18.38	17.76
Elongation at break (%)	640	526	571	345

 Table 4
 Mechanical properties of EPDM/carbon black composites. Reproduced with permission from Ref. [64] Copyright 2008, BME-PT and GTE

black (N330) and the improvement become more significant when mixed filler is used.

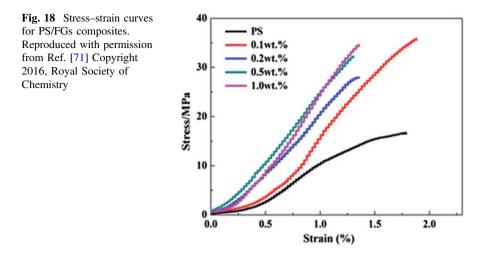
At the loading of 10 phr nanoclay and 20 phr carbon black, tensile strength, elastic modulus, loss factor, and abrasion resistance of the composites increases more compared to 35 phr carbon black filled composite. Also, the thermal stability, thermal conductivity and tensile strength of silicon rubber (SR) increase with increase carbon black (N990) loading. Thus the overall load-bearing capacity of SR/carbon black composite increases [67].

6.3 Graphite and Graphite Nanoplatelets/Polymer Composites

To improve the mechanical property of graphite/polymer composite, graphite is first treated with alkali metals (sodium, potassium, etc.) or halogens and halide ions or with concentrated nitric acid, sulfuric acid, perchloric acid to synthesize graphite intercalated compound (GIC) [68]. Now, this GIC interact better with polymer chains and forms composites having improved load-bearing property. Baptista et al. [69] reported an increase in mechanical properties of epoxy resin with the incorporation of graphite flake (up to 10 wt% loading). Due to greater interplanar distance, graphite nanoplatelets have very high aspect ratio and can be dispersed within the polymer matrix 100 times better than pristine graphite. Liu et al. [27] reported that with the addition of only 7 vol.% exfoliated graphite nanoplatelets (15 μ m) to polyamide 6, flexural modulus increases by 140% and flexural strength increases by 22%. Kim et al. [70] reported that functionalized graphite sheet (FGS) exhibits better improvement in mechanical properties compared to graphite at the similar loading. Poly (ethylene-2, 6-naphthalate) (PEN)/graphite composite shows 17.50% increase in tensile modulus with the addition of 3 wt% graphite whereas for PEN/FGS composite the increase in tensile modulus is 31.50%. It can be concluded that FGS/PEN has better load-bearing characteristics than graphite/ PEN.

6.4 Graphene/Polymer Composites

The exceptional mechanical property of graphene can be utilized to make high load-bearing polymer composites. Wang et al. [71] reported improved load-bearing capacity of functionalized graphene (FGs)/polystyrene (PS) composites where tensile strength increases by 103.7% and tensile modulus increases by 407% with the addition of 0.5 wt% FG (Fig. 18). The resultant mechanical properties are quite higher than that obtained from PS/MWNT or PS/thermally reduced graphene oxide



(TRGO). This result is an indication of effective load transfer between FGs and PS. Fang et al. [72] has shown 70% increase in tensile strength and 57% increase in Young's modulus of 0.90 wt% graphene nanosheets filled polystyrene composite. Achaby et al. [73] reported that with the addition of 3 wt% graphene nanosheets (GNs) modulus and tensile strength of PP/GNs composite increases by 100 and 81% respectively. Also, the thermal stability of the composite increases by 11%. Chen et al. [74] investigated significant improvement in mechanical properties of graphene/polyurethane nanocomposite. According to their observation, tensile strength, modulus, and toughness increases by 51, 105, 48%, respectively. Bera et al. [45] investigated 245% increase in tensile strength, 180% increase in tensile modulus, 5% increase in hardness and 200% increase in toughness of thermoplastic polyurethane (TPU) by incorporating just 0.10 wt% of RGO. There are many other examples where load-bearing capacity of polymers increases with graphene loading.

6.5 Carbon Nanotube/Polymer Composites

Carbon nanotubes are one of the most important CBMs use to increase the load-bearing capacity of polymer composites. Sometimes it is used in unmodified form and sometimes need to modify the surface to increase the interaction with polymers. Surface modification can be done either by functionalization of the surface with hydroxyl, carbonyl, and carboxyl groups or by treatment with strong acids, plasma treatment, etc. [28]. Li et al. [48] reported 228% increase in tensile strength and 1040% increase in Young's modulus of poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer (SEBS), with the incorporation of 15 wt% pristine MWNTs. Pitchan et al. [75] investigated that mechanical

property of polyetherimide (PEI)/MWNTs at 2 wt% loading increases 15% more in cases of acid and plasma treated MWNTs compared to untreated MWNTs. So. surface treatment provides better load-bearing property. Fatigue is one of the major issues for structural failure of composite materials. Zhang et al. [76] reported the suppression of fatigue crack growth rate of epoxy resin by incorporating CNTs. They also observe that the suppression of crack growth rate is dependent on the CNT loading and type of CNT used. For epoxy/MWNTs composite, the reduction of crack growth rate is $\sim 1000\%$ at 0.5% loading of MWNTs. Similar amount of crack growth reduction is observed at just 0.1-0.25% loading of SWNTs. So, SWNTs are more effective than MWNTs. With the help of simulation study, Gavrilov et al. [77] reported that mechanical property of elastomer/CNTs nanocomposites is dependent on the size of CNT used. Another important problem usually encounters with carbon-based polymer composites in the long-term structural application is creep. Zhang et al. [12] reported that creep behavior of thermosetting epoxy resin can be slowed down by incorporating 0.1-0.25 wt% of SWNTs. The epoxy/SWNTs composite can retain very good load-bearing capacity even at higher temperature.

6.6 Carbon Fiber/Polymer Composites

Carbon fiber/polymer composites are mainly used in structural applications for many decades. Since CFs is continuous fiber they can provide very high load-bearing property. One common problem encountered with carbon fiber is the lack of adhesion with polymer matrix. To improve the adhesion between CFs and polymer various sizing materials are coated on CFs surface. Jiang et al. [51] reported improved load-bearing capacity of epoxy resin/carbon fiber composite treated with GO and sizing agent. According to their observation, interfacial shear strength (IFSS) of carbon fiber/epoxy is increased by 37.2% for 2 wt% sizing agent and 1 wt% GO-treated CFs compared to CFs without GO. At this concentration of GO, the interfacial interaction between polymer/modified CFs are maximum and hence, mechanical property is better. Dhakate et al. [49] investigated excellent mechanical properties of carbon fiber semi-aligned electrospun carbon nanofiber hybrid polymer composites. With the addition of 1.1 wt% CNF bending strength increased by 175% and the modulus increased by 200%. Fu et al. [78] reported that at any loading CFs provide better tensile strength and tensile modulus to PP matrix compared to glass fiber (GF). This is probably due to superior mechanical properties of CFs compared to GFs. Creep behavior is very important for a material used in structural applications. Goertzen et al. [79] reported that for CF/epoxy composite, no creep failure occurs within 1600 h when the applied load is 77% of the ultimate tensile strength of the composite. But, with increase in temperature the failure time and load decreases, i.e., the material fails at lower load and within a shorter time. For example, stress requires inducing failure of CF/epoxy composite within 50 years, decreases from 84% of UTS at 30 °C to 42% at 50 °C. Load-bearing

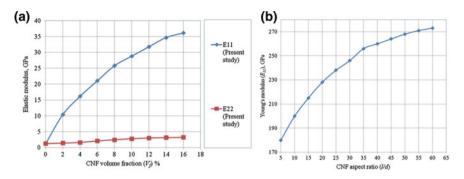


Fig. 19 a Variation of Young's modulus (E_{11} and E_{22}) with percentage of CNF in PP for fixed aspect ratio (l/d) = 10; b variation of Young's modulus (E_{11}) with aspect ratio (l/d) of CNF. Reproduced with permission from Ref. [81]. Copyright 2016, Springer Nature

capacity decreases with increase in temperature. Kawai et al. [80] also investigated the effects of stress ratio and temperature on fatigue life of a carbon fiber-reinforced polyamide-6 composite. According to their observation tensile and compressive strength decreases with increase in temperature from room temperature to 70 °C temperature. Also, the static stress level for a constant value of life under fatigue loading will deteriorate with increase in temperature.

6.7 Carbon Nanofiber/Polymer Composites

Carbon nanofiber (CNF) is one of the most important members of carbon-based filler. It has drawn tremendous scientific attention due to its diverse application opportunities. It can be used in electrical devices, battery, supercapacitors, sensors, structural applications, etc. The one-dimensional nanomaterial has very high aspect ratio ($\sim 250-2000$) [36]. Hence, it can be used in high load-bearing polymer composites. With the help of molecular dynamic simulation, Sharma et al. [81] reported the effect of CNF volume fraction and aspect ratio (l/d) on the mechanical properties of CNF/PP nanocomposites. According to the simulation result, longitudinal modulus (E_{11}) increases with increase in CNF vol.% and at 2 vol.% loading E_{11} of PP increases by 748%. Young's modulus (E_{11}) also increases with increase in aspect ratio of CNF. With increasing the aspect ratio from 5 to 60, E_{11} increases by 48% (Fig. 19).

Although, there is very little effect of CNF volume fraction and aspect ratio on the transverse modulus (E_{22}). In all cases CNF/polymer nanocomposites have lower mechanical properties compared to CNT/polymer nanocomposites. This may be due to lower intrinsic mechanical properties of CNF over CNT [34]. Kumar et al. [82] reported that compressive strength and modulus of PP/nano carbon fiber increases by 100 and 50% respectively at 5% loading of nanocarbon fiber. Similar type of improvement in mechanical property was observed by Zeng et al. [83] for

PMMA/CNF composite. At 5% loading of CNF, axial tensile modulus increases by 50% and compressive strength increases by 170%.

6.8 Fullerene/Polymer Composites

Aggregation of fullerenes is one of the major drawbacks of polymer/fullerene composite. Various physical/chemical modifications of fullerene have been done to improve the thermal, mechanical, electrical, optical, and photovoltaic property of polymer/fullerene composite [31]. Doping of polymers with fullerene (mainly C_{60}) is another emerging area of intense research which improves the load-bearing characteristics of polymer/fullerene composites by efficient load transfer between polymer and fullerene. Rafieeet al. [84] reported improved load-bearing characteristics of epoxy/fullerene nanocomposite. According to their observation, toughness of fullerene/epoxy composite increase by 89%, ductility increases by 35%, Young's modulus increases by 18.5%, tensile strength increases by 20% with the addition of 1 wt% fullerene. The typical stress-strain curve of epoxy/fullerene composites at different loading of filler is shown in Fig. 20a. Crack propagation response of fullerene/epoxy composite at different stress intensity is shown in Fig. 20b. A significant lowering of crack growth rate was observed in fullerene/ epoxy composites. Fracture toughness increases by $\sim 50\%$ with the addition of 1 wt% of fullerene to the epoxy resin which is much higher than that observed in 1 wt % amine functionalized MWNTs filled epoxy resin composite (26% only). So, the fullerene/epoxy composites improve the load-bearing capacity of epoxy resin and become useful in many structural applications like infrastructure, aerospace structure, automotive body parts, etc.

Kim et al. [85] reported the tensile properties and fracture mechanism of a bulk heterojunction (BHJ) films based on PTB7:PC₇₁BM. According to their observation, mixing ratio and amount of additive (1, 8-diiodoctane) play an important role in the tensile property. At higher concentration of fullerene, the composite becomes

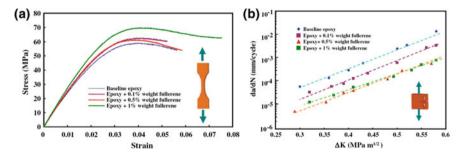


Fig. 20 a Stress-strain curve; b crack growth rate (da/dN) versus stress intensity factor amplitude (ΔK) graph for fullerene/epoxy resin composite at different fullerene loading. Reproduced with permission from Ref. [84]. Copyright 2010, Springer Nature

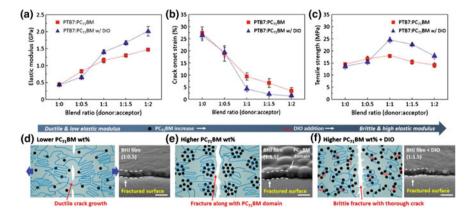


Fig. 21 Tensile properties and fracture mechanism of PTB7:PC₇₁BM blend films as a function of the PC71BM content and DIO additive. **a** Elastic modulus, **b** crack onset strain, and **c** tensile strength of PTB7: PC₇₁BM blend films as a function of blend ratio and DIO additive. Fracture mechanism and SEM images of fractured surface of PTB7:PC₇₁BM bulk heterojunction films with respect to PC71BM content and DIO additive: **d** 1:0.5 blend films, **e** 1:1.5 blend films without DIO additive, and **f** 1:1.5 blend films with DIO additive (scale bar 200 nm). Reproduced with permission from Ref. [84]. Copyright 2010, Springer Nature

stiffer and more brittle and fracture occurs along the aggregated fullerene domains. 1:1 mixture of fullerene and polymer provides the best mechanical properties. The presence of 1, 8-diiodoctane additive increases the stiffness and strength and reduces the ductility further. Tensile properties and fracture mechanism are shown in Fig. 21. Mechanical properties of polymer/fullerene composites as a function of molecular structure are elaborated by Savagatrupet al. [86]. They explored the presence of various pendent groups on the mechanical properties of their composites.

7 Applications

Metal, alloys, wood, and concrete are being replaced by polymeric composite materials in several advanced applications like aerospace, automotive, marine, infrastructure, etc., because of their light weight and superior mechanical properties. Nowadays, the applications of carbon-containing polymer composites are ubiquitous. The diversity in structure and properties of CBMs are reflected in their polymer composites which endow their applications in infrastructure, aerospace structure, automotive body parts, biomedical applications, sports equipment, energy storage, marine structures and others. However, every CBM cannot be used for all these applications. Each CBM has some special structural features which are utilized in some specific applications only. Microcracking and damages are common

problems for these composite materials. Hence, the concept of self-healing become promising for the applications like aerospace, marine, automotive, pressure vessel, and infrastructure where the tendency of cracking and damage are the maximum. Self-healing composite materials are capable to heal or repair the cracks and damages by it and thus extend their shelf life. It also reduces the repairing and maintenance cost of the materials.

7.1 Infrastructure

Infrastructure refers to the fundamental facilities and services offered by a country, city or area for its economic growth as well as to improve the standard of living of people. Infrastructure includes bridges, roads, tunnels, water supply, electrical grids, etc. Reinforced cement concrete (RCC) has the maximum share in this area. Recently, carbon-containing polymer composites stepped into the field because of their high load-bearing capacity and corrosion resistance. Lighter weights of the polymer composites facilitate their transportation quite easily to the working sites. Carbon fiber/epoxy and carbon fiber/vinyl ester resin composites are commonly used in bridge and tunnels. Although, carbon-containing polymer composite has not any problem of rusting like steel cords, used in concrete, economically it is costlier but the bridge made with carbon/polymer composite vibrate too much during the traffic movement which affects in the stability of bridge [13]. Another important problem usually encounters with carbon-based polymer composites in long-term structural application is creep. Zhang et al. [12] reported that creep behavior of thermosetting epoxy resin can be slow down by incorporating 0.1-0.25 wt% of SWNTs. The epoxy/SWNTs composite can retain very good load-bearing capacity even at higher temperature.

7.2 Aerospace Structures

The primary requirement of aerospace structural materials is that they should have low density at the same time should be very strong and stiff. Carbon-based materials have relatively low density and outstanding all-round properties. Hence, these materials can be exploited to make lightweight and high-performance polymer composites which find their applications in aerospace structures. The most important criterion for a polymer to be used in any part of aeroplane structure is that it will not produce any toxic fumes during fire. Carbon-phenolic composites are used in floor and many other inner structures like inner walls, toilet, cubicles, etc., are also made of polymer composite materials. The structure of seats is made up of metals and alloys. But, some aeroplane companies like Boeing, Airbus, etc., have already started making the whole aeroplane structure by carbon/epoxy composite material [87, 88]. For example, in Boeing 787 (Fig. 22), polymer composite

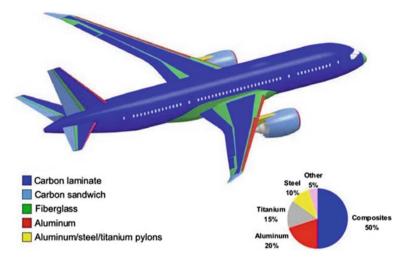


Fig. 22 Application of carbon fiber/polymer composite in Boeing 787 [87]

accounts 50% share of the total materials used which is relatively higher than Boeing 777 where only 12% polymer composite was used. Because of increased percentage of polymer composites, the aeroplane becomes 20% lighter than aluminum designs and also reduces the chances of fatigue failure [88]. Helicopters are mostly made with carbon-containing polymer composite materials. It not only reduces the weight of the whole structure but also increases the performance of the helicopters. Thus, carbon-containing polymer composites slowly replaced the conventional aerospace structural materials like aluminum and alloys. In space applications also composite materials are becoming very important. Rockets structures are made by filament-wound carbon fiber-epoxy composite material. Monetta et al. [89] reported graphene/epoxy anticorrosive composite coating for aircraft structure where only 1 wt% graphene is used.

7.3 Automotive Body Parts

Polymer composites have been a part of automotive industry since 1953 when it was first used in the corvette, small warship. The use of carbon-based polymer composites replaces the conventional materials like steel, aluminum, etc. Polymer composites are relatively lightweight materials with improved strength and corrosion resistance property. But, the cost of carbon fiber based polymer composite is too high (around 10 times higher than glass fibers) that is why they are used only in special cases. Now the challenge is to develop high-strength polymer composite which will be economic as well mechanically strong [11]. Wang et al. [10] reported shape memory induced self-healing property of crosslinked polyethylene/CB

composites. According to their observation, this material can heal the scratches instantly which is an important requirement of a material used in automotive body parts. Bhowmick and coworkers [90] reported significant improvement in thermal, mechanical, and gas impermeability of bromo butyl rubber (BIIR)with the addition of para-phenylenediamine modified graphene oxide (GO-PPD). According to their observation, tensile strength (200%), storage modulus (189%), thermal stability (17 °C), and gas impermeability (44%) increases with the addition of 4 wt% GO-PPD. Hence, this material can be used in tire inner linear and tubes.

7.4 Biomedical Applications

Bone and tissue engineering, drug delivery, and sensor are the three major areas of biomedical emerging. Biocompatibility is the primary criteria of a material to be used in biomedical applications. Among the CBMs, ND, graphene and related materials, CNFs are mostly used in biomedical applications. There is a conflict regarding the biocompatibility of nanodiamond. According to some researchers, detonation nanodiamond has intrinsic biocompatibility while some are saying NDs induce toxicity under certain condition. Schrand et al. [14] reported that NDs has better biocompatibility than carbon black, SWNTs and MWNTs. Sun et al. [15] reported that chitosan (CS)/NDs composites scaffold can be used in bone tissue engineering applications. They measured the important mechanical properties of CS/NDs composites by nanoindentation method and found two important observations: (i) With the addition of 5% NDs, Young's modulus is increased by 340% and the hardness is increased by 120%, (ii) the improvement in mechanical property is less effective for NDs compared to functionalized NDs (F-NDs). Ochiai et al. [16] reported that boron-doped diamond powder (BDDP)-nafion composite made by flexible electrolysis can be used in dental treatment. Liu et al. [17] reported self-healing composite hydrogels based on polyacrylamide and graphene oxide (GO) used in biomedical applications. It can heal the cut surface very quickly and has very high degree of recovery (88%). Shuai et al. [19] reported that GO-reinforced poly (vinyl alcohol) composite scaffold can be used in bone tissue engineering application. 2.5 wt% loading of GO increases the compressive strength (60%), Young's modulus (152%) and tensile strength (69%) of poly (vinyl alcohol)/GO porous composite scaffold (Fig. 23) and make it a potential candidate for bone tissue engineering application. Graphene/polymer nanocomposites are also used as sensor to detect various gases, temperature [20], pressure, pH [21], etc. Li et al. [18] reported that CNF/poly(acrylate) composite can be used as gas sensor. Graphene-based polymer composites are also used in drug delivery and cancer therapy [22].

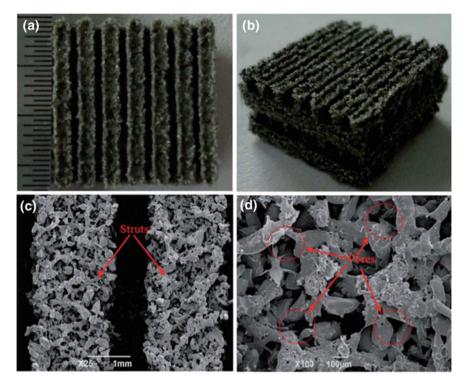


Fig. 23 a, **b** Photographs of the GO/PVA nanocomposite scaffold with 2.5 wt% GO loading fabricated via SLS, **c** the struts of the scaffold, **d** the pores of the strut. Reproduced with permission from Ref. [19]. Copyright 2015, Royal Society of Chemistry

7.5 Sports Equipment

Sporting equipment is an indispensable part of any sport. At the highest professional level of sport, people are ready to pay any amount of money for getting highly advanced equipment. Development of carbon-containing composite materials brings new hope to the athletes. Recently, CBMs/polymer composites are being used to make lightweight, durable and high-performance sporting equipments which reduces the chances of injury and at the same time enhances the performance of the athletes making the sports more enjoyable. Carbon-based materials like graphene, carbon nanotubes, fullerene, nanodiamond, carbon nanofibers, carbon black, etc., are used in sporting equipments like badminton and tennis rackets because of their high strength, stiffness, durability, lightweight, abrasion resistance, etc. Different CBMs have different specialties which are exploited in different sporting equipments as per the requirements. Table 5 shows the specific benefits of using a particular CBM for specific sporting equipments [91, 92].

CBMs	Sports	Benefits
Carbon nanotubes	Tennis/ badminton	Increases strength, stiffness, durability, resiliency, impact, repulsion power and vibration control of rackets
	Golf	Reduce weight, lower torque/spin of the clubs
	Archery	Better vibration control in arrows
Graphene	Tennis/ badminton	Increases strength, stiffness and performance of rackets and decreases the weight. Overall, better control of rackets
	Ice-skidding	Increases strength and durability, decreases weight of skis
	Bicycle race	Increases the strength, durability, decreases the weight of bicycle wheels and safety helmets
	Car racing	Increases the strength, decreases the weight, decreases abrasion and improves the high-speed performance of the car
Fullerene	Tennis/ badminton	Reduces the weight and twisting of racket frames
	Golf	Facilitate flexible club whipping
	Bowling	Reduce chipping and cracking of balls
Carbon nanofibers	Cycling	Reduces the weight and increases the strength and stiffness of the cycle
Carbon black	Road racing	Decreases rolling resistance, increases grip and mileage of tires

 Table 5
 Advantages of using of CBMs for making various sporting equipments [92]

7.6 Energy Storage

Ever-increasing demand for energy and environmental concern has led the scientists to think about the renewable energy technology. It requires a very large number of energy storage devices. Among the currently available energy storage devices, battery, and supercapacitors are most important. They reversibly convert electrical energy into chemical energy. Although, green energy technology like solar energy is also a rapidly growing area where solar cells are being used to convert solar energy into electrical energy. With the advancement of civilization the requirement for smart and portable storage devices like Li-Ion battery [8], high capacity supercapacitor becomes very important. Currently, scientists are working on Li-Ion batteries and supercapacitors to reduce their size and to enhance their energy storage capacity by utilizing graphene. Graphene-based microcapacitor is also a new area of research which may be utilized in smartphones and other small electronic devices. Calixtoet al. [69] reported that graphite powder can be used to make polymer composite with polyurethane, SR and epoxy resin and the graphite/ polymer composites can be used as electrode material. According to their observation best result was obtained at 60 wt% loading of graphite. Fullerene/polymer composites are mostly used in renewable solar energy application. Erb et al. [3] reported that poly(3-hexylthiophene-2,5-diyl)/[6,6]-phenyl C₆₁ butyric acid methyl ester (P3HP/PCBM) films could be used as active layer of plastic solar cells. Mohajeri et al. [4] proposed four fullerene derivatives (Fig. 24) which can act as

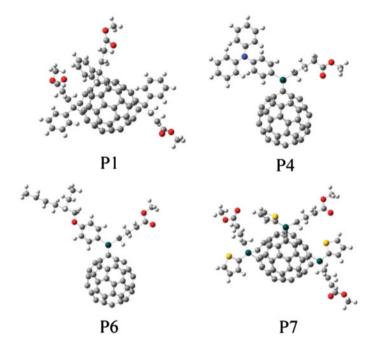


Fig. 24 Structures of fullerene derivatives. C, H, S, N, Si and O atoms are shown in gray, white, yellow, blue, green and red, respectively. Reproduced with permission from Ref. [4]. Copyright 2015, Royal Society of Chemistry

better acceptor than $PC_{60}BM$ in high-performance polymeric solar cells with conjugated polymers, P3HT. Graphene-based polymer nanocomposites are also increasingly used in battery [8] and supercapacitors [9]. Wang et al. [5] reported that polyaniline/graphene hybrids can be used as a counter electrode for dye-sensitized solar cells. The conversion efficiency of the solar cell with this counter electrode reached up to 6.09%. Lin et al. [8] investigated that composite made with 5-sulfoisophthalic acid (SPA) coated silicon nanoparticles doped poly aniline (core/shell SiNPs@PANi/SPA) can be used as anode material of Li-ion battery. It slows down the lithiation/delithiation process and increases the capacity up to 925 mAh g⁻¹ and efficiency of 99.60%.

Savagatrup et al. [6] reviewed about the stability of polymer/fullerene bulk heterojunction solar cells and showed that the stability and performance of the solar cell are dependent on the size and purity of fullerene used. Also, the interaction between the fullerene molecules with the polymer chains plays an important role. Beal et al. [7] reported the morphology of P3HT: PCBM on the performance of BHJ solar cells.

7.7 Marine Structures

Polymer composite materials have been used in marine structure for many decades. They are being used in boats, ships, submersibles, offshore structure and other marine structures like hull, shells, shaft, ducts, etc. The first polymer composite used in marine structure was glass fiber (GF) reinforced unsaturated polyester resin (UPR) composite in early 1950s and continues to be an important material for marine structure. But, there are some disadvantages of using UPR like emission of toxic materials during the curing process can have some serious health and safety issues. Substantial improvement in this field has occurred to tailor the properties and to improve the performance of the composite materials as per the demand of modern technologies. Recently, there is an increasing demand for high-speed marine vehicles (e.g., high-speed boat) where strength and weight of the vehicles are the two most important criteria. Filament wound carbon fibers are mainly used in these cases replacing the glass fibers. Because, carbon fibers provide superior mechanical strength to the boat compared to glass fiber and also lighter in weight. But, carbon fibers are costly. Hence, some balance in cost and properties are required. [93]. Deshmukh et al. [94] reported that GO reinforced poly (3,4-ethylene dioxythiophene)-block-poly(ethylene glycol)(PEDOT-block-PEG)/polyvinylidenefluoride (PVDF)can be used in marine structure because the material has high strength and high corrosion resistance property which fits the marine conditions.

7.8 Pipelines and Chemical Plants

Fiber-reinforced polymer composites are widely used in pipelines, chemical storage tanks, and pressure vessel because of their good mechanical strength, corrosion resistance and chemical resistance property. They can be used to transport or store gaseous chlorine, bromine, carbon monoxide, dilute or concentrated acid and alkalis, etc. Their performance is better than steel. They are lighter in weight, so can be transported quite easily to the site where they need to install. They do not require schedule check-up for corrosion and thus reduces the maintenance cost substantially. Also, the low thermal conductivity reduces the cost of thermal insulation. Excellent load-bearing property is specifically important for chemical storage tank and pressure vessel where high pressure is created. Carbon fibers/epoxy resin is a good combination for this purpose. The electrical conductivity of carbon fiber can be utilized to heat the material by passing electricity through it as and when required. But there is one issue of using carbon fiber which is costly enough [13]. Kotal et al. [90] reported a polymer nanocomposite based on paraphenylenediamine modified graphene oxide (GO-PPD) and bromobutyl rubber (BIIR) which has very high thermal, mechanical and gas impermeability. This material can be used in the inner layer of pipes and pressure vessel.

7.9 Others

Other applications include body armor and in weapons for soldiers, electronic noses, antimicrobial composites, etc. Traditionally metal and alloys are being used in body armor, helmet, arms and transport equipment, etc. Because of the heavy weight of the armor, it reduces the efficiency of the soldiers. Further, the metal parts have an inherent tendency of rusting and corrosion. Hence, carbon–polymer composites have partially replaced the traditional armors. Carbon fiber or carbon nanofiber based epoxy resin composites are mainly used in body armor and in weapons [79]. Polymer composites based of carbon black, PVPD (Poly (Vinyl Pyrrolidone)) and PEG (Poly (Ethylene glycol)) is used as electronic noses (E-nose) which are used to detect various odorant and gases [95]. Santos et al. [96] reported for the first time that with the addition of 3 wt% of GO antimicrobial activity of poly-*N*-vinyl carbazole (PVK)/GO composite increases by 90%. So, the film can be used in antimicrobial composites.

8 Conclusions

Load-bearing capacity is one of the most import properties of polymer composites because it is the basic criteria of a composite material. Together with other parameters, structure of the CBMs and polymers plays an important role in it. The chapter provides state-of-the-art information regarding the load-bearing capacity of different carbon-based polymer composites, load-bearing mechanism, factors influencing the load-bearing property and important applications of load-bearing polymer composites.

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