# Chapter 1
# High-Performance Polymer-Matrix Composites: Novel Routes of Synthesis and Interface-Structure-Property Correlations

**K. A. Dubey and Y. K. Bhardwaj**

**Abstract** No single material or a class of material meets the diverse set of properties required for different applications. Inherent advantages and disadvantages of metals, ceramics, or polymers have made it necessary to develop combinatorial approaches, wherein their functional advantages are maximized and drawbacks are abridged. Composites are the materials comprising two or more constituent materials with significantly different physical, mechanical, electrical, or thermal attributes. Composites offer material characteristics that are different from the individual components and can be engineered to entail synergistic advantages such as high strength, corrosion resistance, electrical or thermal conductivity, and low cost. Notably, in composites, the individual components may remain separate and distinct within the finished structure. The composite material is generally defined by the matrix such as metal-matrix composite, ceramic-matrix composites, and polymer-matrix composites, or by the type and morphological arrangement of the filler such as particle reinforced, fiber reinforced, unidirectional, random, laminates, or honeycombs. Fabrication of composite materials is accomplished by a wide variety of techniques such as melt compounding, in situ polymerization, tufting, tailored fiber placement and filament winding. Depending on the matrix and the filler, different synthetic strategies are adopted. Further with the advent of nano-sized fillers, new class of composites has emerged which have significant important advantages over the conventional composites. This chapter provides details on the synthesis strategies of different polymer-matrix composite materials. A detailed account of the strategies to tailor interfacial adhesion, dispersion, filler asymmetry, filler orientation, and high loading is made, and specific details on the synthesis of nanocomposites and the morphology-interface-property correlation are presented. Recent advances in the theoretical frameworks and the specific applications of the composites are also discussed.

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# Abbreviations

| | |
|---|---|
| 3D | Three dimensional |
| AlN | Aluminum nitride |
| BS | Barium sulfate |
| BT | Barium titanate |
| $CaCO_3$ | Calcium carbonate |
| CF | Carbon fiber |
| CNF | Conducting nano-fiber |
| CNT | Carbon nanotube |
| CPC | Conducting polymer composites |
| DVB | Divinylbenzene |
| EB | Electron beam |
| EPDM | Ethylene propylene diene monomer |
| EPR | Electron paramagnetic resonance |
| Epoxy-Br | Brominated epoxy |
| ER | Epoxy resin |
| EVA | Ethylene vinyl acetate |
| FCE | Fluorocarbon elastomer |
| FRPs | Fiber-reinforced plastics |
| GO | Graphene oxide |
| MA | Maleic anhydride |
| MCFs | Microcrystalline cellulose fibers |
| MMT | Montmorillonite |
| MWCNT | Multi-walled carbon nanotube |
| NCB | Nano carbon black |
| NR | Natural rubber |
| PAN-g-PDMS | Polyacrylonitrile-graft-poly(dimethyl siloxane) |
| PB | Polybutadiene |
| PBA | Poly(butyl acrylate) |
| PC | Polymer composites |
| PDMS | Poly(dimethyl siloxane) |
| PP | Polypropylene |
| PTFE | Poly(tetra fluoro ethylene) |
| PVDF | Polyvinylidene fluoride |
| PVP | Poly(vinyl pyrrolidone) |
| SBR | Styrene-butadiene rubber |
| SEM | Scanning electron microscopy |
| SWCNT | Single-walled carbon nanotube |
| $T_g$ | Glass transition temperature |
| TPC | Thermoplastic composites |

TSCs            Thermoset composites
TiO$_2$          Titanium dioxide
TMPTA        Trimethylolpropane triacrylate

## 1.1 Introduction

Polymer composites (PC) are materials consisting of two or more physically and/or chemically different phases separated by an interface. Synthesis of PC aims at developing advanced materials through a synergistic combination of components with significantly different properties. A judicious combination of fillers and polymer matrices results in PC of bulk properties significantly different from those of any of the constituents. Irrespective of the type of PC, interactions at the interface significantly influence the PC properties. At the interface region of PC, the load is transmitted between the filler and the matrix; hence, it is at the interface that stresses develop during processing or during the service life of the PC. The interface may act as a site for adsorption and nucleation as well. Application of PC particularly advanced polymer composites in high-tech sectors such as aircraft and aerospace manufacturing has brought "interface" at the focus both for the industry and academia. Thus, in the last two to three decades, there has been an increased interest in understanding the filler–polymer interface and its modification [1–3]. The interface was initially visualized as the two-dimensional boundary between adjacent phases in composites where an abrupt change in properties was mandatory. However, now it has been realized that it is not two-dimensional, but a three-dimensional zone where a gradual change in properties from one phase to other phase is observed and a more appropriate term "interphase" has been coined to describe it [4]. This chapter describes various strategies devised and adopted for the synthesis of PC. Choice of fillers and polymers, processing strategies, and interface modification particularly through modification of filler surface for various applications have been discussed in detail.

## 1.2 PC Constituents and Their Modification

### 1.2.1 Fillers

Fillers have different key properties like particle size and shape, density, purity, surface chemistry, thermal, electrical, and optical properties. They were initially employed in PC to reduce material costs and to improve processability. However, the observation that they also alter properties provided an impetus to research on the effect of filler properties on PC. The fillers can be of organic or inorganic origin with geometries like particulates, spheres, fibers, ribbons, flakes, and platelets. Continuous fillers like fibers or ribbons extend throughout the PC in a regular pattern while

discontinuous fillers like flakes, short fibers, and spheres are dispersed throughout the matrix. As the continuous fillers are arranged in a particular pattern/sequence in the matrix, they are also termed as reinforcing fillers. Reinforcing fillers are characterized by the relatively high aspect ratio (*length/diameter*) for fiber or the ratio of diameter to thickness for flakes and platelets. Reinforcing fillers are primarily added to enhance the mechanical properties of the PC, but they may significantly affect other properties such as transparency and thermal stability. Reinforcing fillers sometimes are a major component of the PC. Discontinuous fillers are randomly dispersed in the matrix, and their orientation is governed by the processing and shaping methods. Irrespective of the filler type (continuous or discontinuous), properties of PC are highly dependent on key properties of fillers, the extent of filler loading in PC, type, and extent of interaction with the polymer matrix, and fabrication protocol followed for PC synthesis [5].

### 1.2.1.1  Types and Geometry of Fillers

A wide range of materials like talc, fly ash, glass, inorganic carbonates, synthetic polymer fiber, carbon fiber, sisal fiber, banana fiber, conducting fillers, and agricultural wastes such as crop husk, sawdust, groundnut shell, and aquatic animals shell powder have been used as fillers in PC. An important parameter for evaluating the effectiveness of filler is the ratio of its surface area ($A$) to its volume ($V$). Higher the ratio, the better is the reinforcement [6]. The size of the filler drastically affects the properties of PC. Figure 1.1 illustrates that maximizing A/V and particle/matrix interaction through the interface requires $\alpha >> 1$ for fibers and $\alpha << 1$ for platelets[7]. A report on the effect of addition of micro- and nano-size aluminum nitride (AlN) on properties of brominated epoxy (Epoxy-Br) has clearly shown that nano-AlN



**Fig. 1.1** Plot of the surface area-to-volume ratio ($A/V$) versus aspect ratio ($\alpha =$ length/diameter) for cylindrical particle. "Reproduced with the permission of Elsevier" [7]
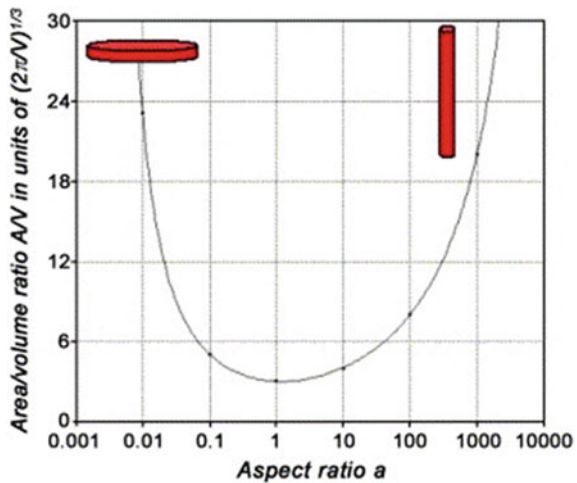
decreases $T_g$ while micro-AIN enhances the $T_g$ of the matrix. The decrease in $T_g$ has been attributed to effective aggregation of nano-AlN and voids in the composites and to decrease in the cross-link density of the epoxy-Br matrix in presence of nano-AlN [8]. Another interesting study on the effect of incorporating micron- and nanometer-sized aluminum particles in polyester resin established that overall fracture toughness increased monotonically with the volume fraction of aluminum particles, for the given particle size, provided particle remains de-agglomerated and dispersed. Also, nanoparticles led to a greater increase in fracture toughness for a given particle volume fraction. Elastic modulus was in accordance with the rule-of-mixtures [9]. Fu et al. critically reviewed the effect of particle size, particle/matrix adhesion, and particle loading on composite stiffness, strength, and toughness of a range of composites having micro and nano-fillers [10]. They report diverse trends of the effect of particle loading on composite strength and toughness are observed due to the interplay between these three factors. However, composite stiffness depends on particle loading, not particle/matrix adhesion. There is also a critical particle size (usually in nanoscale) below which the composite stiffness is greatly enhanced (by the much larger surface area) imparting a nano-effect.

### 1.2.1.2 Filler Surface Modification and Its Effects on Composite Properties

Surface modification of fillers is an easy and reliable method to bring out desired changes at the interface and thus to improve the overall macroscopic properties of composites [11]. The method employed for filler synthesis markedly changes the surface energy. The widely used method for surface modification of inorganic filler is by silane-coupling. The chemistry involved in this modification is a generation of reactive silanol group which undergoes a condensation reaction with other silanol groups to form siloxane linkages. In a recent report on styrene-butadiene (SBR)-based formulation for passenger car tires with ultra-low rolling resistance and high wet-grip performance, it has been shown that the pyrogenic and precipitated silica results in composites of very different properties. On the basis of structural phenomenological modeling using layered fiber model (LFM), it was noted that depending on the filler surface properties in one class of composites, during deformation, polymer chain slips-off from the polymer interphase around the filler particles into the gaps between aggregates, resulting in uniaxially oriented high-strength polymer fibers and significantly high tensile strength of composites [12]. In another investigation, the problem of increasing the adsorptive and adhesive interaction at the phase boundary between a matrix and reinforcing fibrous filler has been successfully addressed by modifying the surface of carbon-reinforcing fillers through plasma treatment [13]. An interesting work on the ferroelectric-relaxor behavior of nano-spun fiber of $Ba(Zr_{0.3}Ti_{0.7})O_3$ (BZT-NF)-polyvinylidene fluoride (PVDF) composite reports enhanced dielectric constant and reduced loss tangents at a low volume fraction of BZT-NF surface modified with poly(vinyl pyrrolidone) (PVP) [14]. Both high-energy gamma radiation and electron beam (EB) irradiation have

been used to modify filler surfaces to overcome organophobic character of inorganic fillers and enhance filler–matrix compatibility. Radiation-induced surface modification of fillers is a chemical-free, clean room temperature process. Thus, no residual chemicals are left for post-modification and also temperature-sensitive fillers can be modified using this method. In a study on radiation-modified fillers, maleic anhydride (MA) was adsorbed on montmorillonite (MMT) surface through ionic interaction. The modified filler was dispersed in polypropylene (PP) followed by EB irradiation. It has been postulated that EB irradiation leads to a covalent linkage between radicals generated on MA (of MMT surface) and PP matrix leading to a significant increase in mechanical properties [15]. The EB irradiation of fillers enhances mechanical properties and tribological properties of composites. It has been reported that the introduction of EB irradiated PTFE in ethylene–propylene–diene–monomer (EPDM) not only enhances mechanical properties but also tribological properties of composites. The friction and wear processes (shown in Fig. 1.2) change drastically for EPDM through breaking adhesive bonds on boundary layers, plastic deformation of the contacting area zones, and plowing due to roughness peaks and wear debris and elastic hysteresis due to damping on the incorporation of irradiated PTFE. The coefficient and specific wear rate of irradiated PTFE-filled EPDM increased with an absorbed dose of PTFE. Increase in absorbed dose also increases the energy dissipation (tan $\delta$) of the composite [16]. Recent work on radiation vulcanization of styrene–butadiene rubber (SBR) silica composites reports use of $\gamma$-ray for grafting of polybutadiene (PB) oligomer on the silica surface. The radiation-grafted silica was
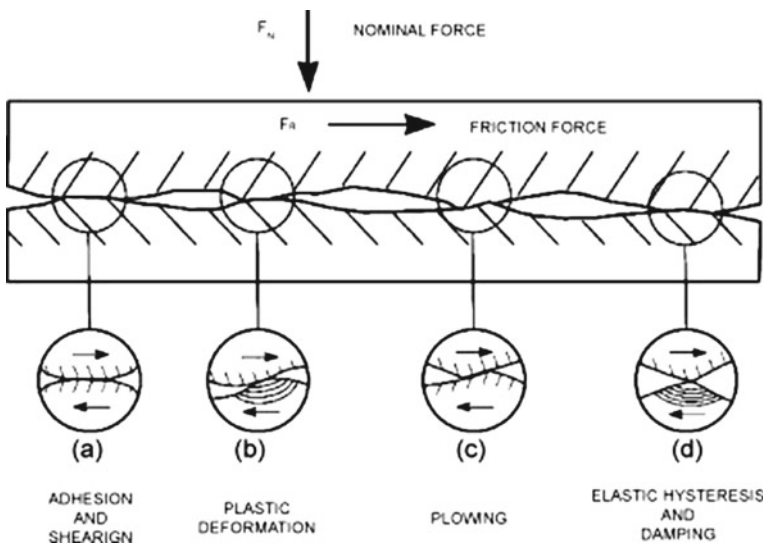


**Fig. 1.2** Friction and wear mechanisms involved in viscoelastic solid bodies sliding against a rough counter surface. "Reproduced with the permission of Elsevier" [16]

dispersed in the SBR matrix. The electron paramagnetic resonance (EPR) investigation indicated that PB coating on silica is effective in enhancing the mechanism of formation of filler SBR covalent links [17]. Gamma-ray irradiation technique was used to functionalize graphene oxide (GO) with alkylamines of various alkyl chain lengths. Scanning electron microscopy (SEM) analysis showed an increase in surface roughness with an increase in alkyl chain length. The addition of alkyl chains on GO surfaces also improved the thermal stability of the GO [18].

## *1.2.2   Polymer Matrix*

The polymer matrix is the continuous component of the composite. Its primary function is to hold the dispersed phase and is usually softer and ductile than the filler. Choice of polymer matrix for the composite depends on the intended application of the composite. The major advantages of polymers, as the matrix, are lightweight, low cost, easy processability, and good chemical resistance. Low modulus and high thermal sensitivity limit their applications [19].

### 1.2.2.1   Types of Polymer for the Composite Synthesis

Almost all type of polymers, thermosetting, thermoplastic, elastomers, or their blends can be used for preparing composites. Thermosetting polymers, e.g., epoxies, phenolics, and melamines, form covalently cross-linked polymer network structures. They decompose on heating instead of softening. Thermosets are commonly used in fiber-reinforced plastics. As initial viscosity of these mixes is low, they are easy to handle. However, as thermoset resins undergo chemical reaction to cross-link the polymer to form three-dimensional (3D) network, a single monolith of filler embedded in 3D polymer network is formed. The 3D network provides dimensional stability, high-temperature resistance, and good solvent resistance. The inherent synthesis process of thermoset composites (TSCs) leads to some design considerations of the finished product. The TSCs are highly anisotropic. As the cured composite itself takes the final structural form, there is poor scope for post-synthesis modification. Recycling of TSCs is energy-intensive and difficult [20]. Thermoplastic polymers are either semicrystalline or amorphous polymers consisting of linear or branched chain molecules. Polyethylene, polypropylene, polystyrene, nylons, polycarbonate, polyether ether ketone (PEEK), etc., fall in this class of polymer. They are characterized by strong intramolecular interactions but weak intermolecular interactions. Elastomers are highly amorphous polymers with glass transition temperature ($T_g$) well below ambient temperature and are thus soft and flexible. They find application as flexible molded parts, sealants, and adhesives. Natural rubber (NR), ethylene propylene diene rubber (EPDM), butyl rubber, polysiloxanes, and fluoroelastomers fall under the elastomer category [21]. A fast-evolving use of elastomers in composites is for electromagnetic (EM) shielding [22], where the introduction of conducting

fillers like graphene and nano carbon black (NCB) negates its insulating behavior and enhances its electromagnetic interference-shielding effectiveness, attenuation, and reflection of electromagnetic waves. The fillers like graphene and carbon nanotube (CNT) could also drastically improve the low stiffness of elastomers. Large volumes of elastomer composite find use as automobile tires. Technologies have been now developed for complete retrieval of different components of used tires leaving the minimal environmental effect of waste tires [23].

### 1.2.3  Interface in Composites

The interactions between filler and polymer matrix at the interface vary considerably from one combination of reinforcement/matrix to others. Interactions at interface have been a debatable proposition. Some groups speculate the formation of primary bonds (covalent and/or ionic) between two phases while others feel that secondary bonding (weak van der Waals interactions) or hydrogen bonding has an important role to play in adhesion of two phases. The interface being a key factor in the performance of composite, rigorous efforts is still on to modify, characterize, and understand it. For a filler–matrix combination, interface is tailored depending on the desired properties of the composite. Interfacial interactions are sometimes so strong that lead to the formation of a distinct phase termed as "interphase." Figure 1.3 illustrates composite interphase [24]. Interphase is as a result of and controls the interaction between filler and the polymer matrix. Strong chemical bonding and relatively weak interfacial bonding would contribute to the improvement in different properties, e.g., in case of structural composites, strong bonding between fiber and polymer leads to increased tensile strength and stiffness, whereas weak interfacial bonding results in better
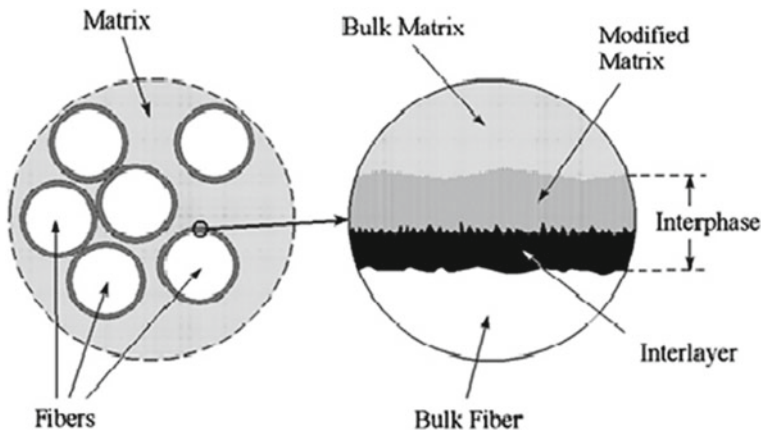


**Fig. 1.3**  Schematic representation of composite interphase. "Reproduced with the permission of Elsevier" [24]

damping characteristics. Interphase no doubt is the fulcrum of the properties of PCs; however, the constituents of PC, the processing protocol followed, and morphology and size of filler are equally important variables that decide final properties of PC. The effect of these variables has been well understood and documented [25–31].

### 1.2.3.1    Interface Modification by Filler Treatment

Certain strategies are adopted to modify the filler surface. The interface tailoring for reinforcing fibers is mainly done by (i) polymer deposition on fiber surface (ii) nanos-tructuring of fiber surface, and (iii) sizing/coating of fiber [2]. The polymer coating on reinforcing fiber surface results in gradient structure at interface, i.e., in such cases the properties gradually change from fiber surface toward the bulk of the matrix (as shown in Fig. 1.3). The polymer coating on fiber surface can be done by polymer grafting, plasma polymerization, or through self-assembly. As the name suggests, polymer grafting involves growing polymer chains on the filler surface. Conventional thermochemical grafting and radiation-induced grafting have been adopted for grafting purpose. Bayley et al. have used a copolymer, polyacrylonitrile-graft-poly(dimethylsiloxane) (PAN-g-PDMS), as fibrous filler for poly(dimethylsiloxane) (PDMS). The graft copolymer was electrospun to produce the fiber filler. It was shown that the PDMS content of the graft copolymer provides increased compatibility with silicone matrices and excellent dispersion of the fiber fillers throughout the silicone matrix. Presence of PAN-g-PDMS as filler further aided the incorporation of multi-walled carbon nanotubes (MWNT) in the composites. The inclusion of PAN-g-PDMS in PDMS in non-woven and aligned forms resulted in significantly different mechanical properties [32]. In another interesting work, microcrystalline cellulose fibers (MCFs), extracted from sisal fibers, were treated with functional end-group hyper-branched liquid crystals (HLP). The treated HLP-MCFs was used for synthesizing HLP-MCFs co-epoxy composites. Even at as low as 1.0 wt% of HLP-MCFs content flexural strength, tensile strength, impact strength, and flexural modulus increased by 60%, 69%, 130%, and 192%, respectively, for the composite [33]. Filler grafted by mutual radiation grafting technique or post-irradiation grafting technique has also shown an effective improvement in many composite systems. Chao et al. report $\gamma$-irradiation grafting of poly(butyl acrylate) (PBA) onto pretreated nano-sized calcium carbonate ($CaCO_3$). The melt compounding of PP with grafted $CaCO_3$ resulted in a synergistic effect, due to the interlayer of grafted PBA between PP and $CaCO_3$. The composite displayed a significant increase in notch impact strength and elongation to break of PP at a rather low content of grafted nano-$CaCO_3$ [34]. An interesting study on EB grafting of fillers reports grafting of trimethylolpropane triacrylate (TMPTA) onto titanium dioxide ($TiO_2$). The effect of modified and unmodified $TiO_2$ onto PP composites revealed, a modified filler not only enhances the mechanical properties significantly but also the reinforcing effect of filler is fully felt even at low filler loading for treated nanoparticles. The EB modification of fillers has many advantages, like a simple process, low cost, ease of control, and having broader applicability [35].

Sizing of filler alters the filler surface and hence the interface. Qing Wu et al. reported the effects of sizing of carbon fiber (CF) using acetone at elevated temperature on the CF-epoxy composite interface. It was shown that up to certain temperature (200 °C), interfacial shear strength of CF-epoxy composite improved markedly post sizing reaction. The interface modulus also increased with a thinner gradient distance. Further increase in surface roughness and a decrease in fiber wettability with epoxy were observed [36]. In other research article influence of sizing components, coupling agents and film formers of glass fiber on the interface of reinforced polyurethane (PU) composites have been reported. The interfacial adhesion properties of untreated, extracted, heat-treated glass fibers, and polyurethane resin were measured through the micro-droplet test. The results showed that the interfacial shear strength of the glass fiber-reinforced PU composite mainly depends on the coupling agents, in which the N-containing groups play a dominant role [37].

### 1.2.3.2   Interface Modification by Matrix Treatment

Altering the interactions at the interface by treatment of matrix is also another potential strategy to enhance filler matrix compatibility. The matrix modification is preferred over filler modification particularly when the filler surface modification conditions are too demanding. It has been reported that compared to conditions for filler modification, the matrix modification involves fewer solvent-based processes [38]. In a recent study, wood polypropylene composites were prepared using polypropylene (PP) modified using divinyl benzene (DVB) and MA to improve interfacial compatibility. It was noted that compared to unmodified PP, composites containing coupling agent or MA modified PP or PP modified by both (DVB and MHA) improved the tensile, flexural, and impact strengths to a greater extent. Interestingly, adding a small amount of DVB (0.4%) resulted in a significant increase in impact strength in comparison with that of the composites modified with only MA [39]. Lai et al. report high permittivity of barium titanate/epoxy resin (BT/ER) composite through graft modification on the ER matrix. Polyether polyols were employed to enhance the molecular polarity of epoxy, which brought more polar oxygen atoms and produced more ester groups in the cured epoxy resin. The permittivity of the composite films containing the same amount of BT fillers improved from 18.91 to 28.73, while the dielectric loss remained nearly unchanged [40]. An excellent article by Gutowski on theoretical principles of macromolecular design of interfaces provides deep insight into contemporary theories on macromolecular "connector molecules." It explains how the chains grafted onto solid polymer surfaces effectively improve adhesion and fracture performance of interfaces. The crux of the investigation is that the interaction between polymers and adjacent material happens through one or both of the following mechanisms (i) chemical reaction/cross-linking with the adjacent material and (ii) interpenetration into adjacent phase. It has been shown that the effectiveness of the interface reinforcement by surface-grafted connector molecules depends on the surface density of grafted molecules, length of individual

chains of grafted molecules, and optimum surface density in relation to the length of connector molecules [41].

## 1.3   Fabrication, Assembly, and Processing of Composites

The fabrication and shaping of composites into finished products often combine the formation of the material itself during the fabrication process. The primary manufacturing methods used to produce composites include manual and automated layup, spray-up, filament winding, pultrusion, and resin transfer molding.

Manual layup is the oldest and simplest method for manufacturing of reinforced products. It involves cutting the reinforcement material to the desired size. The cut pieces are impregnated with a wetting matrix material and spread over a mold surface pre-coated with a release agent. The impregnated reinforcement material is then hand-rolled to ensure uniform distribution and to remove trapped air. More reinforcement material is added until the desired thickness of part has been built up. Manual layup can also be performed using pre-impregnated reinforcement material, called "prepreg." The use of prepreg material eliminates separate handling of the reinforcement and resin. It improves final composite quality but requires stringent process control to prevent premature curing. The throughputs of the manual layup can be increased through machine automation. There is virtually no limit to the size of the work that can be tape-rolled (particularly through automation), but the shape has to be relatively flat to butt each successive layer without gaps or wrinkles [42].

In spray-up, the resin is sprayed onto a prepared mold surface using a specially designed spray gun. This gun simultaneously chops continuous reinforcement into suitable lengths as it sprays the resin. It is suitable for making tub, boats, tanks, and transportation components in a variety of shapes and sizes. Through spray-up, the chopped laminate has a good conformability. It is faster to hand layup method particularly when complex molded shapes are desired. After layup, the composite parts can be cured at room temperature, with hot air, by oven baking, using heated plates or in autoclaves. The curing time depends on the heating method and may range from an hour to a day. Curing can also be accomplished by bag molding in which a non-adhering plastic film is sealed around the layup material and mold plate. Curing is done with heat and pressure, and vacuum is slowly created under the bag forcing it against the layup as a result of which integrated molded part shaped to the desired configuration is obtained [42].

Filament winding is used for the manufacturing of curved/circular surfaces such as pipes, tubes, spheres, cylinders, and construction of large tanks and pipework for the chemical industry. Filament winding is typically applied using either hoop or helical winding. High-speed precise laydown of continuous reinforcement in pre-described patterns is the basis of the filament winding method [42].

Pultrusion is a continuous process used to produce long, straight shapes of constant cross section. Pultrusion is similar to extrusion except that the composite material is pulled, rather than pushed, through a die. Pultrusions are produced using continuous

reinforcing fibers that provide longitudinal as well as transverse reinforcement in the form of mat or cloth materials. These reinforcements are resin impregnated by drawing through a resin mix and shaped within a guiding or performing system. They are then subsequently shaped and cured through a preheated die or set of dies [42].

Resin transfer molding (RTM) has proven to be the most economic process for the fabrication of large, integrated, and high-performance products. In this process, a set of mold halves are loaded with dried, cut reinforcement material shaped into a preformed piece (called preform), and then clamped together. The resin is then pumped or gravity fed into the mold infusing the reinforcement material. Once the mold is filled with resin, it is plugged and allowed to cure. After curing, the mold halves are separated and the part is removed for final trimming and finishing. Reaction injection molding (RIM) is similar to the injection molding except that here those thermosetting polymers are used, which requires a curing reaction to occur within the mold. Here the two parts of the polymer are mixed together, and the mixture is then injected into the mold under high pressure using an impinging mixer. Among polymers, polyurethane (PU) is the most common RIM processable material. If reinforcing agents are added to the mixture of RIM, then the process is known as reinforced reaction injection molding (RRIM). A subset of RRIM is the structural reaction injection molding (SRIM), where meshes are a reinforcing agent. The fiber mesh is first arranged in the mold, and then the polymer mixture is the injection molded over it [42].

Cured composites may be sawed, drilled, or machined to desired dimensions and shape using sharp tools. In view of high abrasiveness of composites, the use of coolant is preferred to avoid heat buildup during machining. Composite parts can be assembled using suitable adhesives producing strong permanent joints. Curing and setting with the pressing of workpieces in a fixture at room temperature or elevated temperature are common practice for composite assembly. Mechanical fastening of joint configurations like a lap, double lap, overlays, and scarf joints using rivets, screws, nut and bolts pins, and other fasteners is also adopted for multi-component composite assembly [42].

## 1.4   Composites and Their Applications

Polymer composites were initially envisaged for lightweight high-strength material but in last two decades, and another genre of composites, namely conducting composites has been the area of active research due to their application as chemiresistive sensors, strain sensors, piezoresistive sensors, electromagnetic interference (EMI) shielding, radio frequency (RF) shielding microelectronics, and antistatic protectors. Conducting polymer composites (CPC) score over intrinsic conducting polymers (polymer with a backbone of π–conjugated electrons) in terms of pronounced mechanical and environmental stability as well as the option of tunable conductivity [43]. Polymers like poly(ethylene) (PE), PP, poly(urethane) (PU), elastomers, conducting polymers, their blends, and fillers like electrically conductive functional

materials like carbon black (CB), carbon fiber (CF), carbon nano-fiber (CNF), single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT), graphene, graphite, metals and metal oxides, and conjugated polymers have been used for composite preparation. Solvent-based as well as solvent facile methods have been practiced for preparing CPC [44]. Preferential percolation is a fast-evolving promising strategy to develop conducting composites at a lower loading of conducting filler. In an interesting development, recently synthesis and characterization of acrylonitrile butadiene styrene (ABS)-polycaprolactam (PCL)-NCB-based conducting composites were reported. It was found that in the composites, ABS and PCL exist as two separate non-interacting phases in which NCB selectively percolates at the interface. The electrical conductivity of the composites as a function of polymer ratio in the composites is shown in Fig. 1.4. Thermal investigation (Fig. 1.5) of these composites established that an optimum composition of composite results in sudden disruption of conductivity depending on $T_g$ of the polymer matrices. Such composites may find application as effective overcurrent protection devices [45].



**Fig. 1.4** Variation of DC conductivity with blend (ABS-PCL) composition for (**a**) 30 wt% NCB and (**b**) 50 wt% NCB. "Reproduced with the permission of John Wiley and Sons" [45]
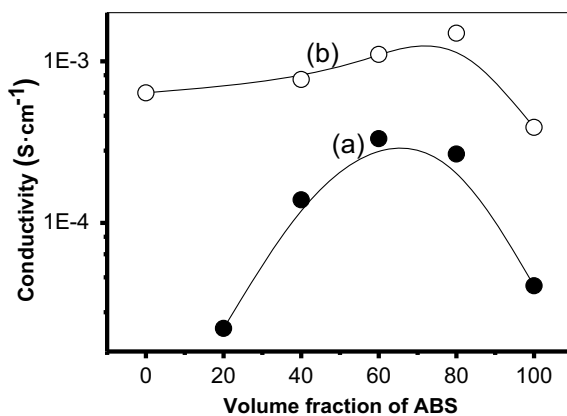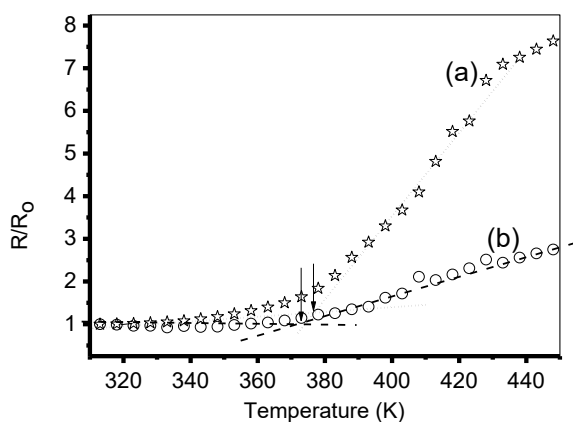


**Fig. 1.5** Abrupt changes in the electrical conductivity of (**a**) ABS/NCB 30 wt% and (**b**) ABS/NCB 50 wt% binary composites; dotted lines represent linear fit in two regions (before and after $T_g$) of ABS and intersection of two slopes that have been shown by arrows. "Reproduced with the permission of John Wiley and Sons" [45]

Radiation has proven to be an effective tool for the synthesis and processing of CPC due to its inherent advantages. Dubey et al. recently reported strain sensing behavior of fluorocarbon elastomer (FCE)-nanocarbon black (NCB) nanocomposites of different network densities [44]. Different extent of cross-linking was achieved by irradiating with high-energy radiation from Co-60 gamma source for different doses. Figure 1.6 shows a synthesis protocol for these composites. The effect of network density on AC, DC conductivity, and electromechanical performance has been reported. Network density was found to have a profound effect on the sensing range as well as on the gauge factor (GF) of the composites (Fig. 1.7). Cyclic strain sensing response was also found to be affected by network density, and the best results were observed for a network density of 73.2 µmol/g. At higher network density (290 µmol/g), two peaks were observed for each strain cycle, and the sensing response was not stable (Fig. 1.8). For 5 and 10% cyclic strains, the gauge factor was around 14, and no change in gauge factor was observed within 2–5 mm/min strain rates [46]. Mondal et al. explored the development of FCE-NCB composite-based novel stand-alone radiation processed chemiresistive sensor with high sensitivity and selectivity for 2-propanone. They report significant, radiation absorbed dose-dependent change
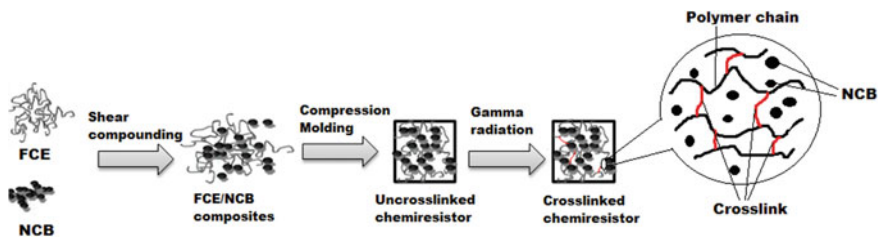


**Fig. 1.6** Schematic of FCE/NCB strain sensor/chemiresistor synthesis protocol (red lines depict cross-linking). "Reproduced with the permission of Elsevier" [48]

**Fig. 1.7** Variation in elongation at break (EB) and gauge factor for nanocomposite with 0.35 weight fraction of NCB with dose. (**a**) Elongation at the break. (**b**) Gauge factor. Inset: change in DC conductivity with the dose for nanocomposite with 0.35 weight fraction of NCB. "Reproduced with the permission of Elsevier" [48]
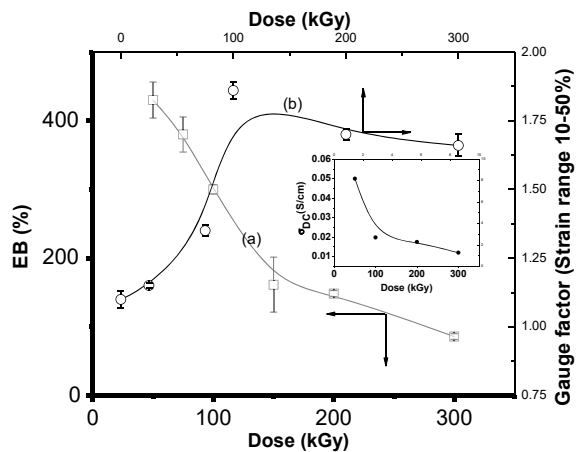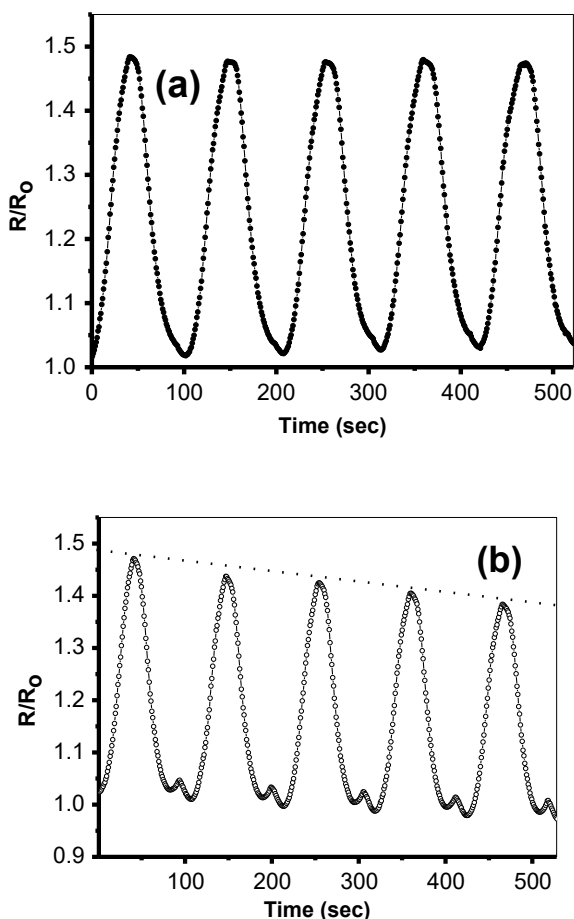
**Fig. 1.8** Sensing response ($R/R_o$) of nanocomposite (FCE-NCB) with 0.35 weight fraction of NCB irradiated to different doses at 5% strain at a strain rate of 1 mm/min. (**a**) 50 kGy, (**b**) 200 kGy. "Reproduced with the permission of Elsevier" [48]



in relative change in resistance ($A_r$) and sensing kinetics of chemiresistive sensors. As shown in Fig. 1.9, the chemiresistor showed linear response with 2-propanone concentration and also highly selective response for 2-propanone in comparison with others like benzene, toluene, xylene, ethanol, methanol, and water (Fig. 1.10) [47].

Certain studies report the synergistic effect of two fillers on composite properties. Hybrid nano-carbons have been reported to have synergetic advantages on several mechanical and electrical applications. Recently, the development of PDMS-CNT-NCB-based novel chemiresistive sensors through a solvent-free route was reported. These sensors demonstrated high sensitivity and reversible response against benzene, toluene, ethylbenzene, and xylene (BTEX) (Fig. 1.11). The sensing response had a strong correlation with BTEX–PDMS interaction parameters ($\chi$). Introduction of CNT in PDMS-NCB composite affected detection of each analyte differently. The principal component analysis using an array of four chemiresistors with different CNT content demonstrated distinct pattern only for benzene. The sensitivity and
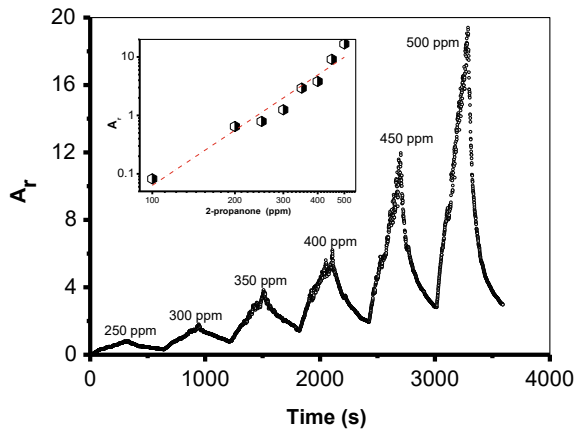
**Fig. 1.9** Variations in the $A_r$ (relative change in resistance; $\Delta R/R_o$) with an increase in 2-propanone concentration (ppm), 2-propanone field nitrogen cycles are shown at each concentration to highlight reversibility [static setup]; inset shows log–log linear fitting. For composite FCE:NCB (65:35) irradiated to an absorbed dose of 100 kGy. "Reproduced with the permission of Elsevier" [47]

**Fig. 1.10** Variation in the relative change in resistance for chemiresistors {FCE:NCB (65:35)} irradiated to an absorbed dose of 100 kGy; [volatile organic compound] = 500 ppm, static setup. "Reproduced with the permission of Elsevier" [47]
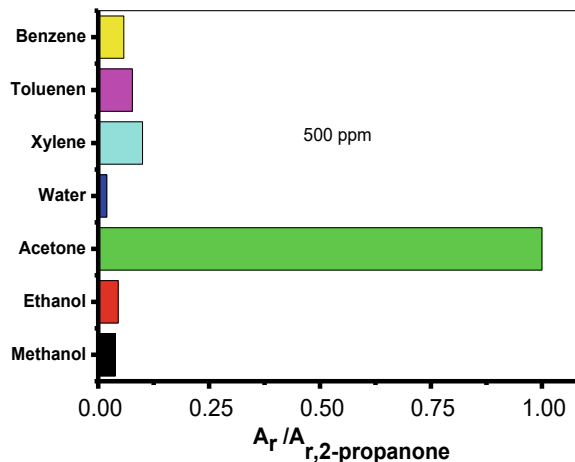


the temperature coefficient of resistance of chemiresistors decreased; whereas, the detection range increased considerably with the addition of CNT [49]. Majji et al. report radiation degradation of Teflon scrap to micro-fine powder and utilization of this polytetrafluoroethylene micro-powder (PTFEMP) for the synthesis of EB cross-linked PDMS-PTFEMP composites [47]. A linear increase in modulus up to an optimum cross-linking dose is reported. As shown in Fig. 1.12, the introduction of PTFEMP did not affect the surface energy of PDMS but significantly reduced the coefficient of friction of the composites [50]. Exceptional synergistic effects between organic–inorganic dual filler in ethylene-vinyl acetate (EVA) composites have been
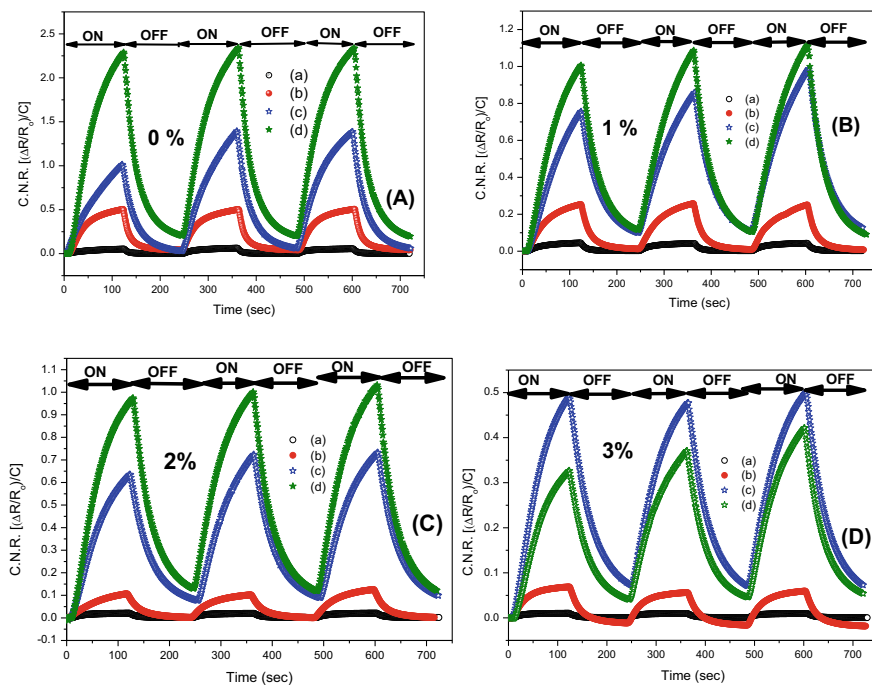
**Fig. 1.11** Concentration normalized relative change in the resistance [CNR = $(\Delta R/R)/C$, $\mu$L/L] for PDMS-NCB: 70:30 nanocomposites (**a**) Benzene. (**b**) Toluene. (**c**) Ethyl benzene, (**d**) Xylene. (**A**) 0 wt% CNT, (**B**) 1 wt % CNT, (**C**) 2 wt% CNT, (**D**) 3 wt% CNT BTEX flow rate = 100 ml/min. "Reproduced with the permission of Elsevier" [49]



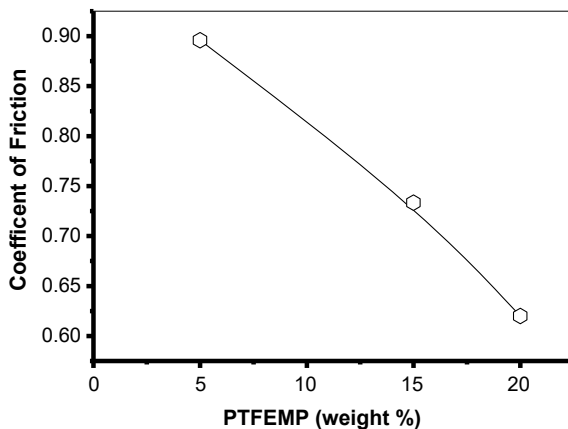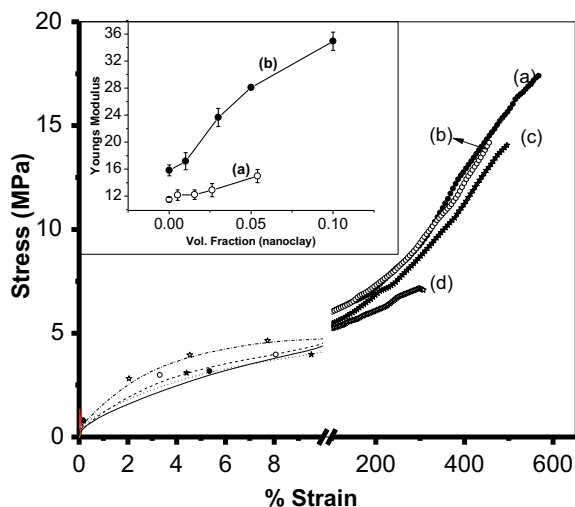**Fig. 1.12** Coefficient of friction PDMS-PTFEMP composites

**Fig. 1.13** Stress–strain profiles for EVA/organoclay (5%) composites having different loading of PTFEMP (**a**) 5%, (**b**) 10%, (**c**) 20%, (**d**) 50% inset: effect of organoclay loading on modulus (**a**) EVA, (**b**) EVA/PTFEMP (15%) composites. "Reproduced with the permission of Elsevier" [51]



observed. Composites of EVA containing PTFEMP and organoclay were prepared by melt compounding. The exceptional increase in the mechanical properties of ternary composites demonstrated high synergy between fillers, leading to a manifold increase in the modulus of dual filler-filled composites in comparison with single filler-filled systems (Fig. 1.13). X-ray diffraction studies revealed ~10% intergallery expansion in organoclay, in the composites having a high loading of PTFEMP; though no significant change in the crystallinity of EVA was observed [51].

Composites are not confined to applications like improvement in mechanical properties or electrical applications. They have been extensively investigated for other applications particularly biomedical applications. $MgSO_4$-EVA composites were found to function as a wide range (15–4000 Gy) absorbed dose dosimeter for industrial radiation processing (Fig. 1.14). During post-irradiation, the electron paramagnetic resonance (EPR) signal of the composite dosimeters faded by ~20% in a month's period. The energy dependence response of the dosimeter was within acceptable limits [52, 53]. Composites of high-density fillers have been investigated for applications involving high-energy attenuation. Recently, interesting findings on EVA-$BaSO_4$ (EVA-BS) composite as highly radiopaque flexible polymer composites for X-ray imaging application have been reported. As shown in Fig. 1.15a, 0.7-mm-thick sheet of EVA-BS composites had markedly higher gray value (radiopacity) than 1 mm sheet of aluminum while retaining more >1200% elongation at break and complete flexibility [54]. On similar lines, Dubey et al. reported studies on radiation cross-linked PDMS-$Bi_2O_3$ composites. As shown in Figs. 1.16 and 1.17, the composites were highly flexible and showed effective attenuation of low-energy (Am-241; 59.9 keV) γ-rays [55].

**Fig. 1.14** Effect of the absorbed radiation dose on the peak-to-peak amplitude of the EPR signal ($A_{pp}$) of the composite (EVA:MgSO$_4$: 50:50): (**a**) 500 Gy to 4 kGy, (**b**) 10 Gy to 500 Gy. "Reproduced with the permission of Elsevier" [52]
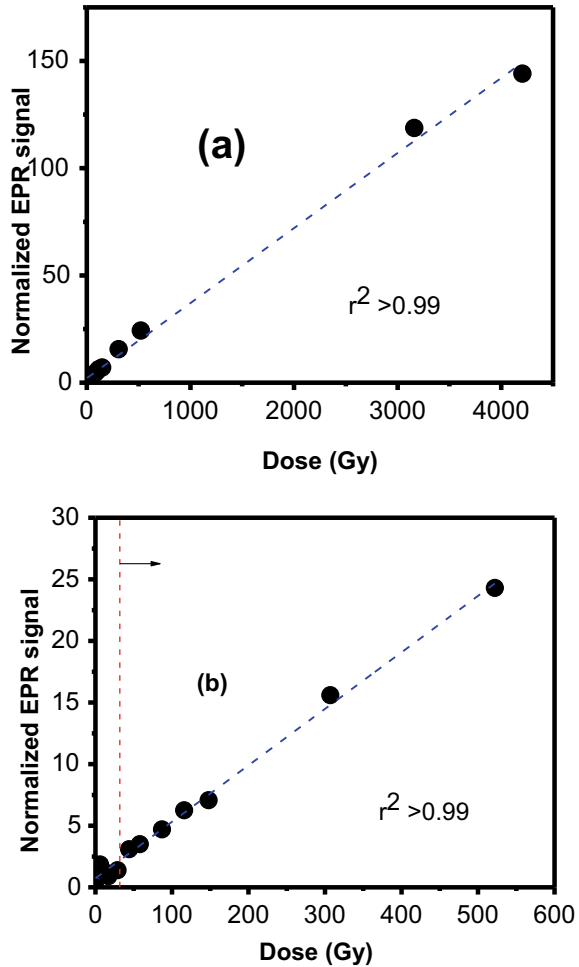


## 1.5 Smart Composites

The current focus of composite research is on the composites which would mimic biological composites. These composites in addition to the desired role (say the increase in mechanical properties) would also be able to sense the damage and undergo self-healing. Thus, in this approach self-sensing of damage in composites employs the reinforcing fibers as the sensing element, obviating the need for the addition of sensing elements to the composite. The concept involves monitoring overall strain in the composite unit in terms of overall resistance or conductivity in the form of an electrical signal. An interesting investigation on this concept is of laminate composites of fiber-reinforced plastics (FRP) proposed for a high-end application like aerospace. Zhang et al. have reported the utility of an embedded CNTs network in
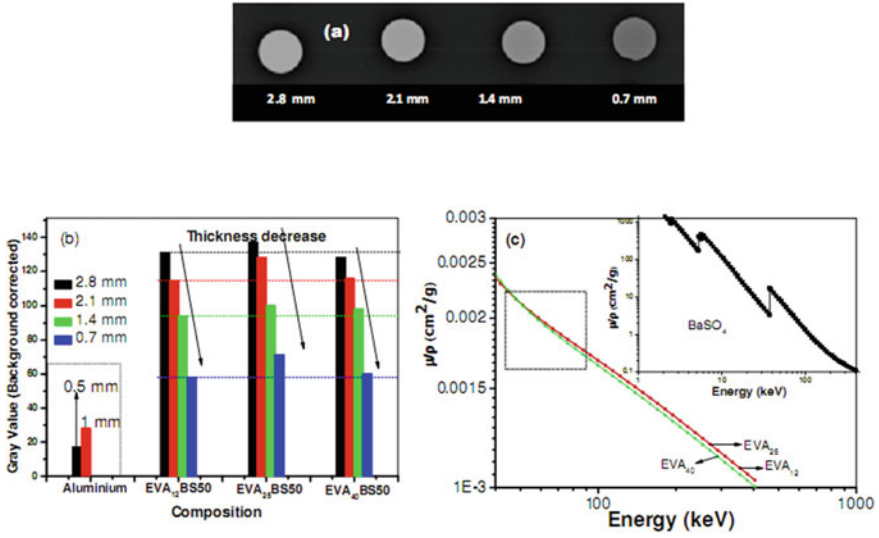
Fig. 1.15 Radiopacity of the composites. (a) Actual X-ray radiographs of EVA$_{25}$:BS (50:50) composites of different thicknesses. (b) Variation in gray values for composites with composition; dotted block presents gray values for aluminum sheets. (c) Variation in mass attenuation coefficient variation of EVA$_{12}$, EVA$_{25}$, and EVA$_{40}$ with X-ray energy (inset: variation in the mass attenuation coefficient of BS with X-ray energy). "Reproduced with the permission of Elsevier" [54]



Fig. 1.16 Flexible radiation shield composite of PDMS-Bi$_2$O$_3$ (30:70). "Reproduced with the permission of John Wiley and Sons" [55]

**Fig. 1.17** Variation in attenuation of different composites irradiated to different doses. Inset: variation in counts with Bi$_2$O$_3$ (weight %) at two different radiation doses. "Reproduced with the permission of John Wiley and Sons" [55]
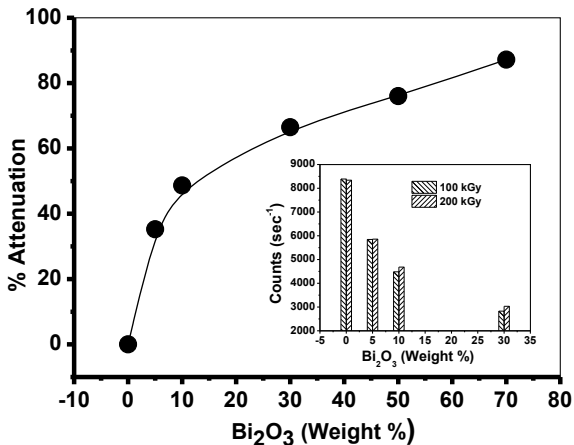


FRP for sensing wear and tear in FRP. It was shown that change in the propagating wear and tear (displacement) with applied stress disturbs the continuity of embedded CNT network proportionately which is reflected as change is resistance of the FRP. Thus, such introduction of CNT into FRP composite provides not only integrated damage sensing capability but also leads to additional mechanical reinforcement [56]. Another study on self-sensing composites for impact damage detection reports the use of commercially available *E*-glass fabric as sensing as well as reinforcing agent for commercial resin-based composite. The extent of damage induced in the panel can be monitored visually or by light transmission. The system is capable of detecting low-energy impacts within the panel. The progression of damage could also be monitored, and multiple impact damage events could also be observed. It was shown that this system is capable of not only identifying and locating the impact but can also quantify the extent of damage within the composite [57]. A notable feature of assemblies/components made from such composites is that non-destructive (NDT) inspection is required which otherwise results in significant reduction in downtime of the system.

Irrespective of the composite application once cracks or faults have formed, the integrity of the structure is significantly compromised. Therefore, to avoid drastic deterioration in properties, the next logical step would be the initiation of a self-repair mechanism on sensing the fault. In fact, the autonomic healing concept was successfully demonstrated at the beginning of the twenty-first century by incorporating a microencapsulated healing agent and a catalytic chemical trigger within an epoxy matrix [58]. An excellent review on the topic appeared recently [59]. As the interface is often the weakest region in composites where failure starts, therefore, it is obvious that self-healing action originates from the filler–matrix interface. In this respect, two distinct approaches are generally followed [2].

(i) **Capsule-based healing systems**: In capsule-based self-healing systems, the healing agent is in the form of discrete capsules. The damage to composite

ruptures these capsules to release the contents at the interface. Thus, if debonding between filler and matrix causes weak load transfer, the repair mechanism rejuvenates bonding and hence the efficient load transfer.

(ii) **Intrinsic self-healing behavior**: Here reversible physical and chemical reactions are exploited to bring out the repair. These physical/chemical reactions are triggered by damage itself or some time by an external stimulus. Predominantly, processes like reversible polymerization, hydrogen or ionic bonding, molecular diffusion causing entanglements, and melting of a thermoplastic phase are involved in self-healing. The healing processes may happen in conjunction also as all of them are reversible events.

## 1.6   Outlook and Future Trends

Composite materials have boundless engineering application where the strength-to-weight ratio, low cost, and ease of fabrication are required. For certain applications, the use of composite materials as compared to metals has in fact resulted in savings of both weight and cost. Polymer composites have been considered among the five synthetic materials that will shape the future of the world. Presently, among the different materials used by the aerospace industry, a large proportion represents fiber-reinforced composites. It is believed that as the cost of these composites decreases, they will find wider applications in automobile and other sectors. Nanocomposites would also not remain confined to presently envisaged applications like lightweight sensors, wind turbine blades, powerful batteries, body scaffolds, etc., because they still are crude in comparison with natural composites which possess incredibly complicated and intricate structure. As the nanocomposite synthesis processes become more refined, it will be possible to design them in a very controlled manner.

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