Deba Kumar Tripathy
Bibhu Prasad Sahoo *Editors*

Properties and Applications of Polymer Nanocomposites

Clay and Carbon Based Polymer Nanocomposites

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With 105 Figures and 11 Tables

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Preface

Nanotechnology is one of the most emerging areas of current research and development due to its vast applications in engineering sectors. Polymer nanocomposites occupy a special position due to their wide range of application. The significant difference between the properties of the neat polymers and their corresponding polymer nanocomposites is due to the remarkable effect of the nanofillers on the polymer matrix. It has been recognized that polymer nanocomposites are very important materials for coating, adhesive, pharmaceutical, biomedical, environmental, automobile, and dielectric applications.

This volume aims to provide information on polymer nanocomposites with special reference to specific application spread over nine chapters. ▶ Chapter 1 of the book is subdivided into two parts. Part (a) provides the information on the introduction to clay and carbon-based nanofillers, their synthesis, and manufacturing technique. Part (b) of this chapter deals with the processing and characterization of polymer nanocomposites. ▶ Chapter 2 explains the application of polymer nanocomposites for electronics, dielectric, and microwave field. ▶ Chapter 3 describes the use of polymer nanocomposites for structure and construction applications. ▶ Chapter 4 discusses the importance of polymer nanocomposites for biomedical and biotechnology applications. ▶ Chapter 5 describes the role of polymer nanocomposites for environmental use. ▶ Chapter 6 deals with polymer nanocomposites for energy and fuel cell applications. ▶ Chapter 7 explains the applications of polymer nanocomposites in automobile engineering field. ▶ Chapter 8 describes how polymer nanocomposites are extensively used for adhesive, coating, and paint applications. Finally, ▶ Chap. 9 deals with applications of polymer nanocomposites for shape memory use.

This volume can be used as a research book for M. Tech Plastic Engineering, Rubber Technology, and Material Science on polymer composites. Also this book can serve as a useful reference for academicians, researchers, materials scientists, engineers, and professionals in polymer and related industries. Therefore, it is hoped that this book will inspire and enthuse to undertake research in the field of nanocomposites.

The editors acknowledge Springer for giving this opportunity and for their enthusiastic and professional support. Finally, we would like to thank all the chapter authors for their contribution for this book.

October, 2015

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Contents

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Introduction to Clay- and Carbon-Based Polymer Nanocomposites: Materials, Processing, and Characterization

1

(a) Synthesis and Manufacturing of Nanomaterial (Nanotube, Nanofiber, Nanoclay, Graphene, etc.) (b) Processing and Characterization of Polymer Nanocomposites

Bibhu Prasad Sahoo and Deba Kumar Tripathy

1.1 Introduction

Nanotechnology is one of the most emerging areas of current research and development due to its vast applications in engineering sectors. Polymer nanocomposites occupy a special position in the field of nanotechnology for their potential applications. The significant difference between the properties of the neat polymers and their corresponding polymer nanocomposites is due to the remarkable effect of the nanofillers on the polymer matrix. The nanostructured materials such as layered silicate (LS), carbon nanofiber (CNF), carbon nanotube (CNT), and graphene are mostly incorporated, for the preparation of multifunctional polymer nanocomposites. The active reinforcing nanofillers are specifically important for the preparation of polymer nanocomposites because of their tremendous enhancement in material properties of the polymer matrix. The aspect ratio (length to diameter ratio), unique microstructure, and surface area for enhancement of the nanofillers make them suitable reinforcing fillers for the development of high-performance and multifunctional materials.

The extent of improvement in the properties of the nanocomposites depends on the several factors such as size of the nanoparticles, aspect ratio, degree of dispersion, and orientation in the polymer matrix and the interfacial adhesion. The strong interfacial adhesions due to the chemical and physical linkages in between the base

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matrix and the nanofillers play an important role on the material properties of the resulted nanocomposites. Keeping these in mind, the melt intercalation process is widely employed for preparation of same.

Recently, the polymer/layered silicate (PLS) nanocomposites have brought about tremendous improvement in material properties as compared to the conventional micro- and macrocomposites. These improvements include high moduli, increased strength, and increase in thermal stability and decrease in gas permeability and flammability. Although, the layered silicate-reinforced polymer nanocomposites have been known a long time, the field of PLS nanocomposites has gained momentum very recently. The nylon-6/layered silicate nanocomposites were prepared by Toyota research group for the first time with pronounced improvements in thermal and mechanical properties. Toyota industry has utilized the nylon-based PLS nanocomposites in the automobile sector where the part of the automobile requires the mechanical strength and thermal stability.

(a) **Synthesis and Manufacturing of Nanomaterial (Nanoclay, Nanotube, Graphene, etc.)**

1.1.1 Nanoclays (Layered Silicates)

Nanoclay is one of the most affordable materials that have shown promising results in preparation of polymer nanocomposites for various applications. The commonly used layered silicates for the preparation of PLS nanocomposites belong to the same general family of 2:1 layered phyllosilicates. Their crystal structure consists of layers made up of an inner octahedral (O) layer of aluminum and magnesium hydroxide sandwiched between the two tetrahedral (T) layers of silicone atoms. Figure 1.1 shows the chemical structure of the layered silicate. The unit cell formula is $Na_{0.4}[Si_8]$ $[Al_{3.6}Mg_{0.4}]O_{20}(OH)_4$, where the first and second bracket terms refer to ions in the tetrahedral and octahedral sheets, respectively. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery spacing. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns, depending on the particular types of layered silicate. It consists of silicon oxide (SiO_2), aluminum oxide (Al_2O_3), and magnesium oxide (MgO), which is classified as montmorillonite (MMT), saponite, hectorite, vermiculite, mica, talc, and kaolinite depending on the composition, structure, and layer ratio. The isomorphic substitution within the layers (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}, or Mg^{+2} replaced by Li^{+1}) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries. MMT has platelet structure with average dimension of 1 nm thick and 70–150 nm wide, and it is mostly favored among the nanoclays for the fabrication of polymer nanocomposites because of its high cation exchange capacity (CEC) and adsorptive property. MMT is a member of the smetite class of 2:1 phyllosilicate group of layered silicate with a characteristic repeating distance (gallery spacing) between T-O-T layers [96Gia].

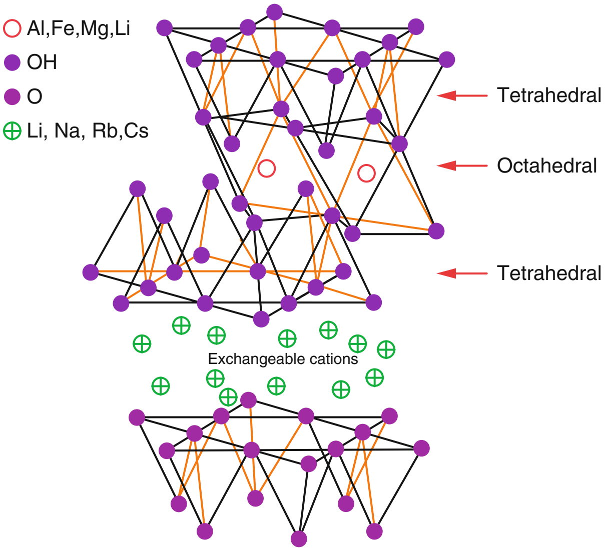


Fig. 1.1 Schematic diagram of layered silicates

1.1.1.1 Modification of Nanoclay

Pristine-layered silicates usually contain hydrated Na^+ or K^+ ions. Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as fluoropolymers, polyethylene oxide (PEO), polyvinyl alcohol (PVA), etc. However, maximum polymers are hydrophobic in nature, and to get both miscibility and compatibility with the base polymer matrix, the LS should be modified and converted into hydrophobic. Generally to increase the interlayer basal spacing between the two conjugative platelets (intercalation) and to establish possible interfacial adhesion between the many engineering polymers and the LS, the LSs are organically modified. Basically, the exchangeable alkyl ions such as Na^+ and Ca^{2+} present in between the layer silicates are exchanged by the cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium, alkyl phosphonium, and alkyl sulfonium organic surfactants. The modified LSs are known as organically modified montmorillonite (OMMT). Figure 1.2 shows the schematic representation of modification of nanoclay. Specially alkyl ammonium or alkyl phosphonium cations form organically modified LSs with low surface energy and improve the wetting characteristics of the polymer matrix and result in a larger interlayer spacing. The inherent ability of the LSs to disperse into individual single layers is an exciting feature for the fabrication of polymer nanocomposites. Additionally, the alkyl ammonium or alkyl phosphonium cations functionalize the LS, resulting in some chemical linkage at the interfacial region.

Nowadays, several pristine and organoclays are available commercially at relatively low cost. Commercially available organoclays include Cloisite® 10A, 15A, 20A, and 30B which are the products of the Southern Clay Products; Bentone® 107, 108, 109, and 2010 which are the products of Elementies Specialist Company;

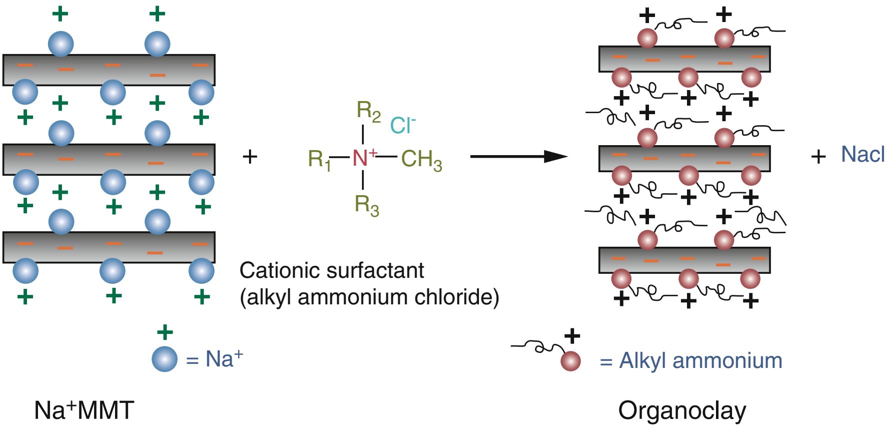
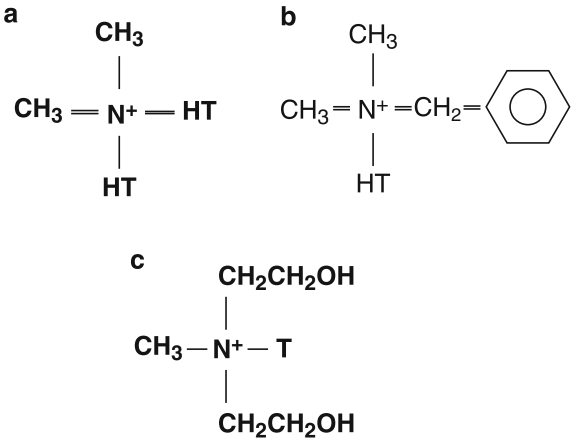


Fig. 1.2 Schematic representation of modification of layered silicates

Fig. 1.3 (**a**) Dimethyl dihydrogenated tallow quaternary ammonium salts, (**b**) dimethyl-hydrogenated tallow quaternary ammonium salts, (**c**) methyl tallow bis-2-hydroxyethyl ammonium



Nanomer® 1.30P, 1.31PS, 1.44P, 1.44PS, 1.44PT, and 1.28E which are the products of Nanocor, USA; and Nanofil 2, 5, 9, SE 3000, and SE 3010 which are the products of Sud-Chemie, Germany. Cloisite 10A contains dimethyl, benzyl, and hydrogenated tallow quaternary ammonium salts (2MBT). However, Cloisite 15A and Cloisite 20A are nonpolar Na$^+$-MMT clays modified with dimethyl dihydrogenated tallow quaternary ammonium salts (2M2HT). HT stands for the hydrogenated tallow-based compound containing ~65 % C18, ~30 % C16, and ~5 % C14, and the major double bonds of this moiety are hydrogenated. Cloisite 30B is a polar organoclay with the organic modifier methyl tallow bis-2-hydroxyethyl ammonium (MT2ETOH), and the formula is shown in Fig. 1.3. Here T stands for tallow group. The respective basal spacing (d_{001}) of the Cloisite 15A, 20A, and 30B are 3.23, 2.42, and 1.85 nm, respectively. The proper selection of organoclay depends on the type of polymer matrix used.

1.1.2 Carbon Nanotube (CNT)

The CNT has proved tremendous importance among the scientific community in the present decade because of their wide range of potential applications in several areas since its invention by [91Iij]. CNT has proven to be very effective nanofiller for its high aspect ratio, low density, and high surface area. A CNT is hundred times stronger and six times lighter than steel and exhibits good electrical and thermal conductivities. CNT is stronger than steel, lighter than aluminum, and more conductive than copper, which can conduct electrons over a long tube length without any significant scattering. It has an excellent combination of mechanical, electrical, and thermal properties that make CNT a potential candidate to substitute the conventional nanofillers in the fabrication of multifunctional polymer nanocomposites (PNC). CNTs are long cylinders of covalently bonded carbon atoms. The ends of the cylinders may or may not be capped by hemifullerenes. It is an allotropic modification of carbon, and the extraordinary properties of the CNT are attributed to the unique tubular structure of the graphitic sheets, which is in the order of nanometers in diameter and microns in length. The carbon–carbon (C–C) chemical bond present in CNTs is completely formed by sp^2 hybridized bonding orbitals, which is comparatively stronger than the sp^3-type bonding structure located in diamond; as a result, it exhibits extremely high mechanical properties [99Sal]. Depending on the reaction conditions of fabrication techniques, there are two basic types of CNT: single-wall carbon nanotubes (SWNT) and multiwall carbon nanotubes (MWNT) as shown in Fig. 1.4. MWNT is considered to be the most versatile nanomaterial due to its high flexibility, low mass density, high aspect ratio (typically $>10^3$), and exceptional mechanical, thermal, and electrical properties.

The SWNT is made up of a single sheet of graphene layer, which is perfectly folded to form a hollow cylinder with a diameter in order of 1 nm and up to few centimeters in length [93Iij]. The MWNT consists of more than single concentric cylindrical graphene layers with an interlayer spacing of 0.35 nm (equal to the basal plane separation in turbostratic graphite), which are coaxially assembled around the central main hollow core by the van der Waals force of attraction between the

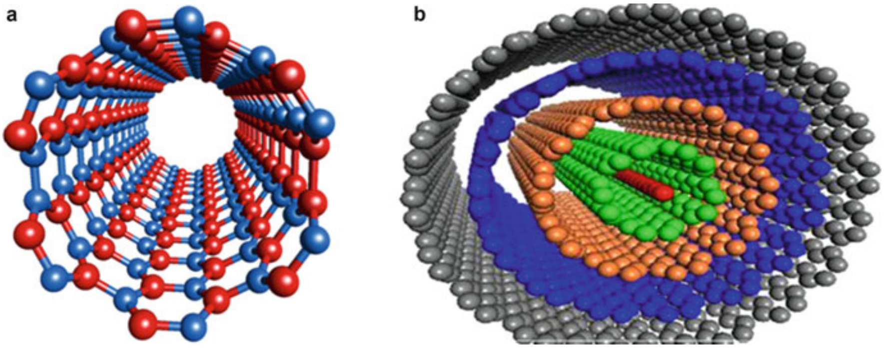


Fig. 1.4 (**a**) Single-walled nanotube and (**b**) multiwalled nanotube

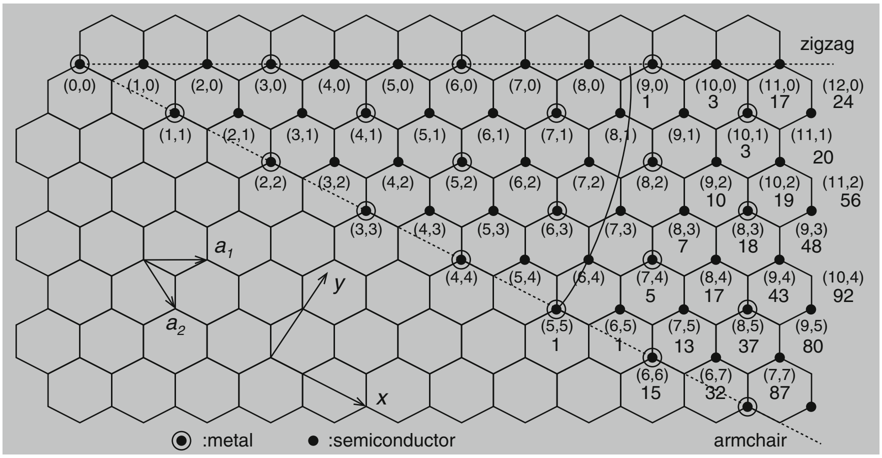


Fig. 1.5 Pictorial representation of chiral vectors of graphene sheets for formation of different types of SWNT

adjacent graphene layers [91Iij]. MWNT has diameters ranging from 2 to 10^2 nm and lengths in tens of microns. The whole families of CNTs are classified into three types of tubes of different diameters based on the rolling up of the graphene sheets along one of the symmetry axis (armchair and zigzag tubes) or in a direction that differs from a symmetry axis (chiral tubes) [00Odo]. Figure 1.5 shows the pictorial representation of chiral vectors of graphene sheets for formation of different types of SWNTs. Different synthesis techniques adopted for production of CNTs in large quantities [93Bet] are direct current electric arc discharge, laser ablation, high-pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD). However, the most common commercial practice for cost-effective production method for CNT fabrication is undoubtedly CVD, which develops CNTs having a very huge amount of defective sites. The functionalization of carbon nanotubes is carried out by different conventional (covalent, non-covalent exohedral, and endohedral functionalization [05Hir]) and nonconventional (radiation-induced graft polymerization (RIGP), plasma treatment [05Fel], and γ–irradiation [04Ska]) methods to improve its solubility, wetting, dispersion, processability, and properties.

The pristine CNTs have enormous prospect for extensive application in conductive plastics, energy storage, sensors, electronic devices, electron microscope tips, electron emission devices, structural materials, catalyst supports, biological applications, air and water filtration, ceramics, and so on [01Tho]. The MWNT is an ideal reinforcing nanofiller to develop a new-generation high-strength, light-weight, and multifunctional polymer nanocomposites for electromagnetic shielding, antistatic coatings, high-strength low-density corrosion-resistant components, and light-weight energy storage applications [06Coe]. The electrical conductivity of individual SWCNT depends on their chirality, and it exhibits up to10^6 S/m electrical conductivity at room temperature.

1.1.2.1 Modification of CNT

CNTs, being inert in nature, tends to form entanglement with each other and thus difficult to disperse well in the organic matrices in their pristine states. The surface modification of the CNT is thus very much essential in order to enhance their dispersion in the organic phase. Among the techniques of surface fictionalizations, non-covalent means of surface modifications are quite common. This non-covalent mode of nanotube fictionalization has received a lot of academic [06Fak] interest, which keeps the original CNT's properties intact. In this methodology, the polymer chains are wrapped around the CNT phase, and various surfactant molecules are adsorbed on the surface of the nanotube. [06Zhu] reported the non-covalent fictionalization of CNT based on the colloid stabilization principles, and in this approach, charged inorganic ZrO_2 nanoparticles were used as stabilizing media. Polymer wrapping method is reported by [02Oco] for the non-covalent fictionalization of polymer CNT. Apart from polymer layer medications, the coverage of the CNT surfaces with an inorganic silica layer has also been reported by Li et al. (2006), and the generated silica layer is bound non-covalently to the CNT. The functionalization of CNT with layers of SiO_2 also facilitates the further modification of the CNT surface by utilizing the surface reactions available for silica surface.

In covalent modification, the pendent groups like carboxyl, derivative of carboxyl, hydroxyl, amine, halogens, etc. can be developed on the surface of the CNT. However, in the nanocomposites, for imparting better performance of the CNT phase on the base polymer matrix, the uniform dispersion of the CNT phase is very much required, and it plays a vital role in the overall material properties of the resulted nanocomposites. Specific ionic liquids are used as dispersing as well as coupling agent between the CNT surface and the base polymer matrix. A series of ionic liquids, such as 1-allyl-3-methyl imidazolium chloride (AMIC), 1-ethyl-3-methyl imidazoliumthiocyanate (EMIT), 1-methyl-3-octylimidazolium chloride (MOIC), 3-(triphenylphosphonic)-1-sulfonic acid tosylate (TPST), and trihexyltetradecyl phosphonium decanoate (TTDPD), are used along with CNT for uniform dispersion, and the choice of the ionic liquid depends on the nature of the base polymer and rubber matrix [09Das]. Prior to the incorporation of MWNT, it is first dispersed in ethanol with 1 millimole of ionic liquid per gram of MWNT and sonicated for 2 h to break the MWNT agglomerations. The dispersion of MWNT in ethanol with and without ionic liquid is shown in Fig. 1.6. The MWNT agglomerates are clearly visible in Fig. 1.6a, which represents the sonicated MWNTs in ethanol. However, in Fig. 1.6b and c, no such MWNT agglomeration is found, and these figures represent the dispersed MWNT in ethanol in presence of AMIC and MOIC ionic liquids, respectively. Ionic liquids also act as a coupling agent in between the CNT and polymer matrix.

1.1.3 Graphene

Graphene is the most emerging and advanced multifunctional nanomaterial, which is composed of pure carbon, with atoms arranged in regular hexagonal pattern in a

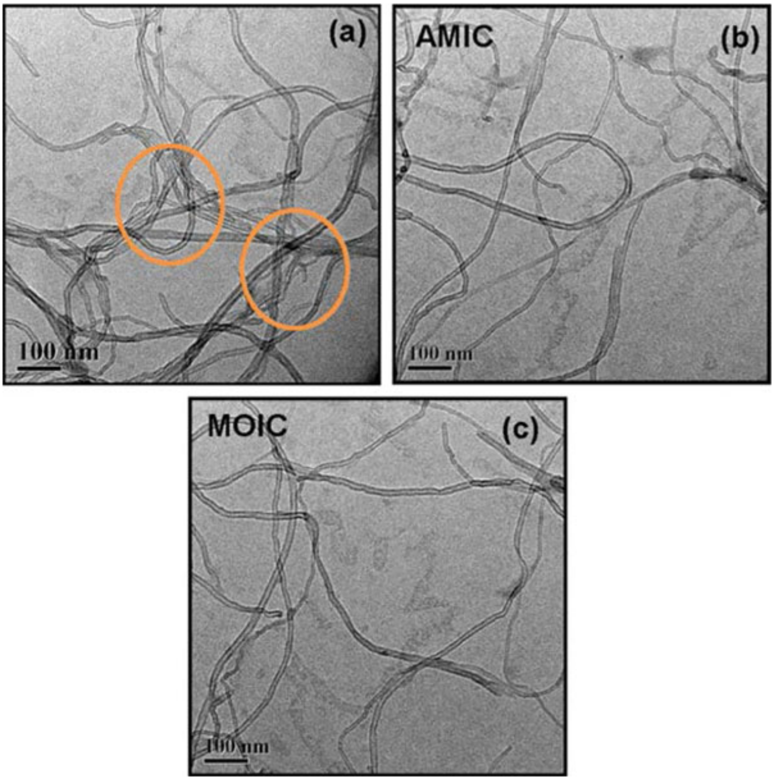


Fig. 1.6 (**a**) Agglomerated MWNT, (**b**) dispersed MWNT in the presence of AMIC, and (**c**) dispersed MWNT in the presence of MOIC

one-dimensional sheet. It is the basic structural unit of some carbon allotropes, including graphite, carbon nanotubes, and fullerenes whose structure is a single planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It can also be considered as an indefinitely large aromatic molecule (benzene rings). The rolling up of graphene along a given direction can produce a carbon nanotube which is very light, with a 1 m^2 sheet weighing only 0.77 mg. The crystalline or flake form of graphite consists of many graphene sheets stacked together. The carbon–carbon bond length in graphene is about 0.142 nm. Graphene sheets stack to form graphite with an inter-planar spacing of 0.335 nm. Depending on the research group, the graphene layer thickness ranges from 0.35 to 1 nm relative to the SiO_2 substrate [05Nov]. Figure 1.7 shows the schematic representation of the graphene sheet. A zero-dimensional fullerene can also be obtained by wrapping up graphene. In 1940, it is established theoretically that graphene is the building block of graphite. The single layers of graphene are identified by a simple tabletop experiment, which were previously considered to be thermodynamically unstable and could not exist under ambient conditions. The promising mechanical, electrical,

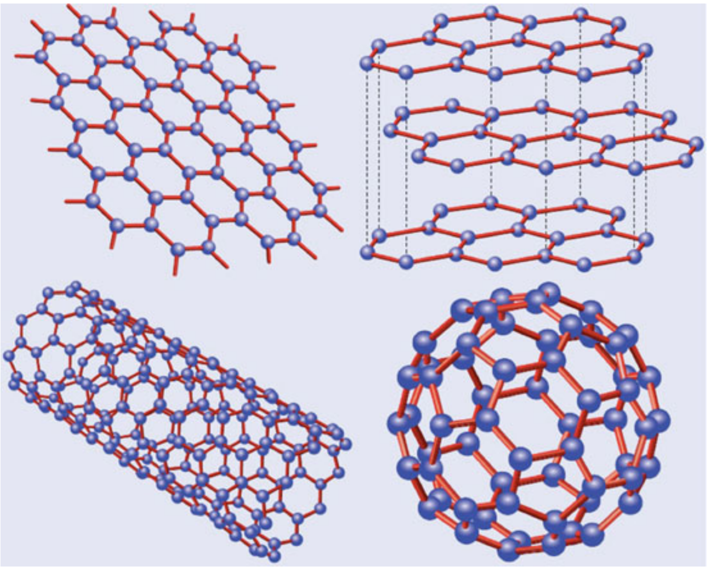


Fig. 1.7 Schematic representation of the graphene sheet

optical, thermal, and magnetic properties of graphene have led to the creation of a new and exciting research field.

Graphene can be prepared using four different types of methods:

The first is chemical vapor deposition (CVD) and epitaxial growth, such as the decomposition of ethylene on nickel surfaces.

The second is the micromechanical exfoliation of graphite, which is also known as the scotch tape or peel-off method.

The third method is epitaxial growth on electrically insulating surfaces, such as SiC.

The fourth one is the solution-based reduction of graphene oxide. It exhibits unique properties such as quantum Hall effect (QHE), higher carrier mobility at room temperature (~10,000 $cm^2/V/S$), large theoretical specific surface area (2630 m^2/gm), good optical transparency (~97.7 %), high Young's modulus (~1 TPa), and excellent conductivity (3000–5000 W/m/K).

1.1.3.1 Surface Modification of Graphene

Pristine graphene materials are unsuitable for intercalation by large species, such as polymer chains, because graphene as a bulk material has a pronounced tendency to agglomerate in a polymer matrix. It is likely that the oxidation followed by chemical functionalization will facilitate the dispersion and stabilize the graphene to prevent agglomeration. The functional groups attached to graphene can be small molecules or polymer chains. The chemical functionalization of graphene is a particularly attractive target because it can improve the solubility and processability as well as

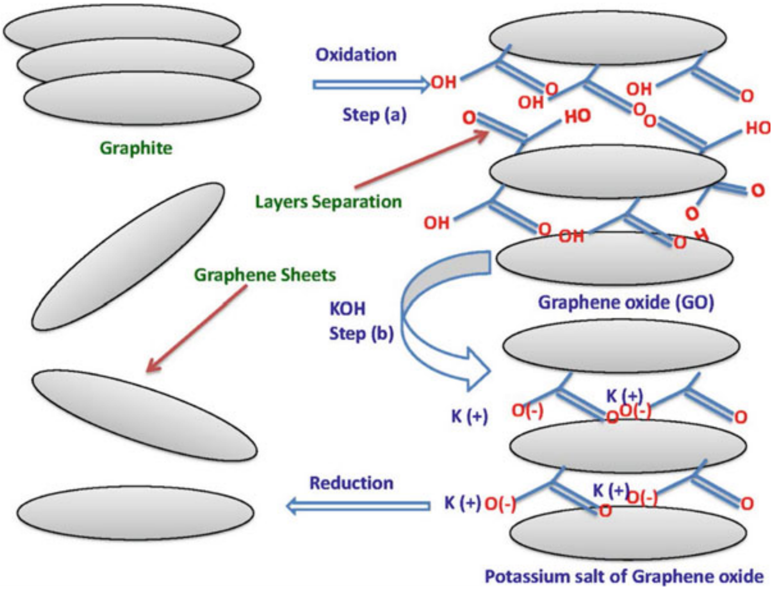


Fig. 1.8 Schematic representation of modification of graphene sheets

enhance the interactions with organic polymers. Considerable works have been carried out on the amination, esterification, isocyanate modification, and polymer wrapping as routes for the functionalization of graphene. The electrochemical modification of graphene using ionic liquids has also been reported. Park et al. [12Par] reported a simple route for the preparation of homogeneous aqueous suspension of chemically functionalized graphene with enhanced dielectric properties. In this process, the precursor graphene oxide is first dispersed in the water medium followed by addition of aqueous KOH. KOH produces a large number of negative charges through the reactions between the reactive hydroxyl, epoxy, and carboxylic acid groups on the base graphene sheets resulting in extensive coating of the graphene sheets with negatively charged and K^+ ions. The addition of hydrazine monohydrate to the suspension of graphene makes a stable colloid of graphene sheets through the electrostatic stabilization. The scheme of the above explanation is shown in Fig. 1.8, Table 1.1.

(b) Processing and Characterization of Polymer Nanocomposites

The nanofillers have strong tendency to aggregate due to their large surface area. These aggregates can be separated by applying high shear force. However, the high shearing of the properties of the nanofillers may deteriorate. Therefore, the biggest challenge is to get a fully dispersed nanofiller in the polymer matrix. Several methods have been successfully adopted to obtain uniform dispersed nanofillers

Table 1.1 Comparison of material properties

Materials	Tensile strength	Thermal conductivity (W/mk) at room temperature	Electrical conductivity (S/m)	Reference
Graphene	130 ± 10 GPa	$(4.84 \pm 0.44) \times 10^3$–$(5.30 \pm 0.48) \times 10^3$	7200	[07Li, 08Bal, 08Lee, 09Lia]
CNT	60–150 GPa	3500	3000–4000	[00Yu, 07Itk, 07Li, 10Spi]
Nano-sized steel	1769 MPa	5–6	$1.35 \times x10^6$	[07Shi, 09Lew]
Plastic (HDPE)	18–20 MPa	0.46–0.52	Insulator	[09Chr, 95Woo]
Natural rubber	20–30 MPa	0.13–0.142	Insulator	[08Sun, 10Mat]
Kevlar fiber	3620 MPa	0.04	Insulator	[09Ven]

in the polymer matrix which include dry powder mixing, solvent casting, melt intercalation, in situ polymerization, and nonionic and ionic surfactant-assisted mixing.

Solvent Casting This is the most common technique for the preparation of polymer nanocomposites. In this method, a suitable solvent is chosen with requisite amount of nanofiller in which the polymer matrix is fully soluble. The benefit of solvent casting is rigorous mixing of nanofiller in polymer followed by ultrasonication which facilitates the nanofiller deaggregation and uniform dispersion. This method follows three steps: in the first step, the dispersion of nanofillers in a solvent is done by ultrasonication; in the second step, the polymer solution is made using the same solvent by a magnetic stirrer separately and mixing of these two solutions followed by rigorous stirring in a certain period of time; and in the last step, the recovery of the nanocomposites is done by casting of film in a hot air vacuum oven in which the solvent is evaporated which results the nanocomposites. Both organic as well as aqueous solvents have been used to produce nanofiller reinforced polymer nanocomposites. To minimize the aggregation of nanofiller, the nonionic and ionic surfactants have been used nowadays. The ionic surfactants sometimes act as coupling agent between the polymer matrix and nanofiller phase.

Melt Intercalation The solvent casting technique is not suitable for bulk industrial-scale process, and the organic solvents used here are highly flammable. Therefore, for mass scale production of polymer nanocomposites, the melt intercalation technique is a most preferable one. The melt intercalation technique is abundantly used due to its technically viability, versatility, environmentally friendly characteristics and good compatibility with the conventional polymer processing techniques. This is the most popular technique for the preparation of thermoplastic nanocomposites. This technique has become the standard method for the preparation of polymer nanocomposites and adopted by the commercial industries due to its easy processability and cost-effectiveness. This technique involves the melting of polymer granules to form a viscous liquid and application of high shear force to disperse the nanofillers. The chemical structure and melt viscosity of polymers influence the molecular diffusion and shear stress during melt mixing, which governs the nanostructure morphology of the polymer nanocomposites. The melt viscosity of the base polymer and elastomer plays a vital role in the dispersion of nanofiller in polymer matrix, and the shear stress inside the mixing chamber affects the melt viscosity abruptly. Haake Rheocord and Brabender Plasti-Corder are the most common internal mixing machines used in melt intercalation techniques to fabricate polymer nanocomposites with enhanced properties than corresponding the unfilled polymers. However, in this process, high shear force and high temperature deteriorate nanocomposites' performance properties due to fragmentation of nanofillers.

In Situ Polymerization Recently, in situ polymerization technique has been extensively explored for the preparation of polymer-grafted nanofiller nanocomposites. The main advantage of this technique is that it enables the grafting of macro-sized polymer molecules on the surface of the nanofillers. In addition, the in situ polymerization technique is a suitable processing method, which allows the processing of nanocomposites with high nanofiller loading and with very good dispersibility. This technique is very much suitable for the processing of insoluble and thermally unstable polymers which are very difficult to process by solvent casting and melt intercalation technique. When the nanofiller is LS sheets, the polymerization occurs in between the intercalated LS sheets. At first the swelling of the LS occurs within the liquid monomer and polymerization initiates either heating or radiation by incorporation of suitable initiator. This technique is first successfully applied in manufacturing of nylon-MMT nanocomposites by Kojima et al. [93koj], and latter it is extended for other thermoplastic polymers. This method is more convenient for the preparation of thermoset resin-clay nanocomposites.

1.1.4 Polymer/Layered Silicate (PLS) Nanocomposites

The thickness of the layered silicates is found to be around 1 nm, and they are having varying aspect ratios (10–1000). Very little amount of LS can be dispersed throughout the polymer matrix due to its high surface area. Depending on the strength of interfacial interactions between the polymer matrices, three different types of PLS nanocomposites are thermodynamically obtained which are flocculated nanocomposites, intercalated nanocomposites, and exfoliated nanocomposites. The schematic representation of the three different types of morphology of the nanocomposites has been shown in the Fig. 1.9.

Sometimes flocculated morphology is observed in the nanocomposites, and this is due to the nonuniform dispersion of the nanoclays within the viscous polymer matrix. The LS contains hydroxyl groups in its edge and due to the hydroxylated edge-to-edge interaction in terms of hydrogen bonding of the LS agglomerates. The

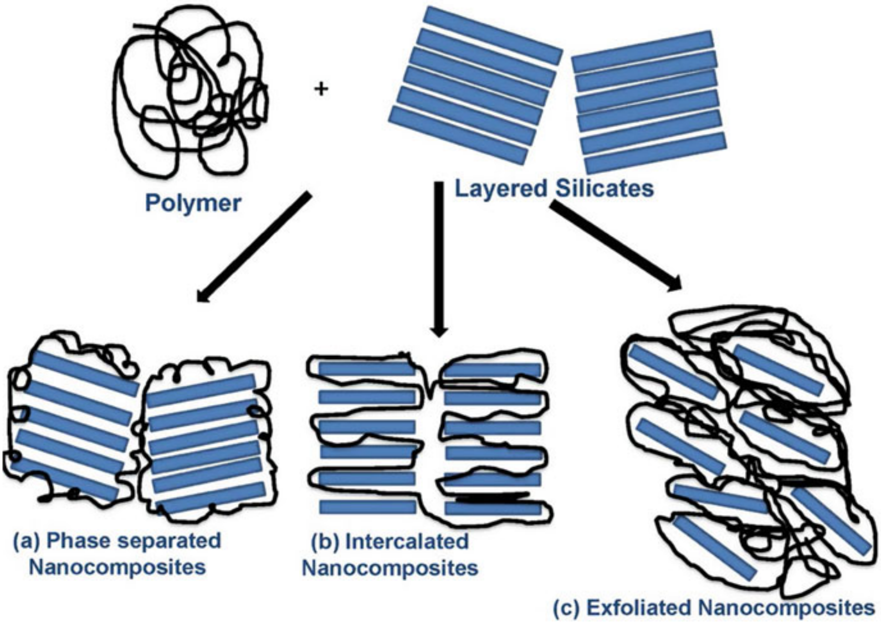


Fig. 1.9 Schematic representation of (**a**) phase-separated, (**b**) intercalated, and (**c**) exfoliated polymer nanocomposites

schematic picture of flocculated LS in polymer matrix is shown in Fig. 1.9a. In intercalated nanocomposites, the insertion of polymer chains between the two LS layers in a regular crystallographic fashion results in a well-ordered multilayer structure of alternating polymeric and LS with a characteristic repeating distance between them. The schematic diagram of the intercalated phase morphology has been shown in Fig. 1.9b. Exfoliated or delaminated phase morphology is observed when the individual clay layers are separated from one another and individual clay platelets dispersed in the continuous polymer matrix, and the average distance depends on the clay loading. The schematic picture of the exfoliated phase morphology is shown in Fig. 1.9c. The exfoliation or delamination configuration is of particular interest because it maximizes the polymer–nanoclay interaction making the entire surface of layers available for the polymer. This could lead to the most significant changes in mechanical and physical properties.

1.1.5 Effect of Layer Silicates on the Performance Properties of Polymer Nanocomposites

In the area of nanotechnology, polymer matrix such as epoxies, thermoplastic polyurethanes, thermoset polyurethane, polyimides, nitrile rubber, polyesters, styrene butadiene rubber, polyolefins, polystyrene, and polysiloxane-based nanocomposites

Table 1.2 Mechanical and thermal properties of nylon-6/clay composites (Kojima et al., 1993a, b, c)

Composite type	Wt% of the clay	Tensile strength (MPa)	Tensile modulus (GPa)	Impact strength (kj/m^2)	HTD (°C) at 185 kg/cm^2
Exfoliated nanocomposites	4.2	107	2.1	2.8	145
Micro-tactoids	5.0	61	1.0	2.2	89
Neat polymer	0.0	69	1.1	2.3	65

have drawn a significant amount of attentions. The use of organically modified LS as precursors in the fabrication of nanocomposite has been used with various polymer systems due to their significant improvement in the performance. To exhibit better performance of the nanocomposites, the clay platelets must be uniformly dispersed (exfoliated) in the polymer matrix instead of tactoid agglomerations and intercalation. Exfoliated LS platelets result in the improvement in mechanical properties, enhancement in barrier properties, decrease in solvent uptake, increase in thermal stability, and flame retardance [98fuk] which is due to nano-reinforcement effect. Complete uniform dispersion of the LS in a polymer matrix optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. The coupling effect of the clay platelets have extremely high surface area (760 m^2/g), and the polymer matrix facilitates the easy stress transfer to reinforce the polymer phase results the improvement in the tensile and toughness properties. However, in conventional polymer/LS, composites containing the agglomerated nanolayer tactoids ordinarily improve rigidity, but they sacrifice the strength, elongation, and toughness. The remarkable improvement in performance of the exfoliated nylon-6/LS nanocomposites has been observed by Kojima et al. [93koj] as shown in Table 1.2.

In the early 1990s, Toyota research group first reported work based on the nylon-6/LS nanocomposites and reported significant improvement in mechanical properties in terms of mechanical modulus and tensile modulus at a loading level of only 4.2 wt% of LS. Properly aligned clay platelets have proved to be very effective for increasing stiffness, and the common reason for this improvement in the modulus and stiffness is due to the reinforcing effect imparted by the properly dispersed and aligned clay platelets. The nanoclay-filled nylon-6 nanocomposites exhibit two times more tensile modulus than the neat nylon-6. It is observed that to achieve similar properties, nylon-6/glass fiber composite need three times more mass of glass fiber than montmorillonite (MMT) platelet nanocomposite. Thus, the nanocomposite has a weight advantage over the conventional glass fiber composites. In case of LS-filled nanocomposites, the clay platelets are aligned in the plane of the resulted nanocomposites, and the same reinforcement is observed in all directions within the plane. However, the glass fibers reinforce only along a single axis in the direction of their alignment. Another important aspect of the reinforcement is due to the better surface finishing of the nanocomposites than that of the glass fiber-reinforced composites. The impermeable clay layers mandate a tortuous/zigzag pathway for the stress transfer in the nanocomposites. The polymer/LS nanocomposites exhibit

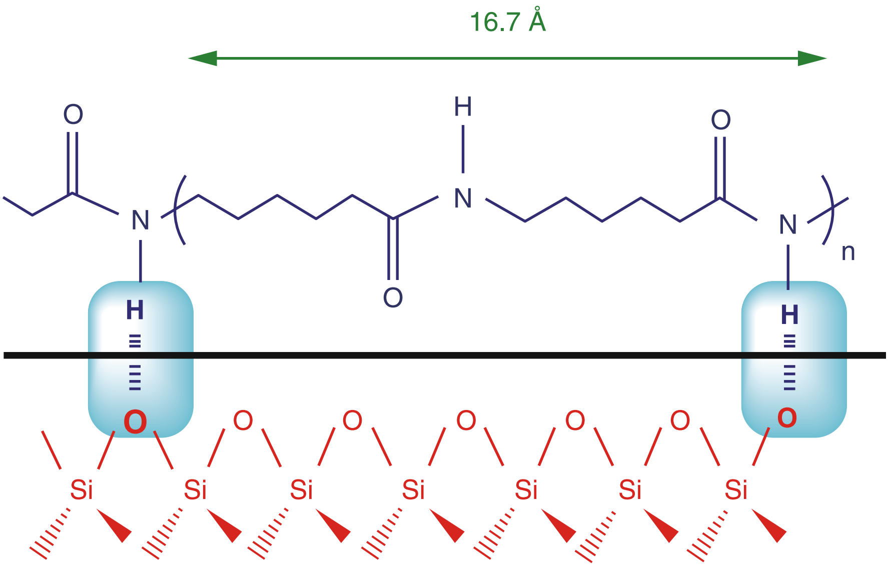


Fig. 1.10 Schematic representation of the formation of hydrogen bonds in PA6– pristine MMT

enhanced barrier characteristic, chemical resistance, reduced solvent uptake, and flame retardance properties, and the clay platelets hinder the diffusion pathways due to the nucleating effect. Fornes et al. [04For] investigated the effect of the structure of alkylammonium compounds on the dispersion of MMT in polymer-6 during melt compounding. They found that quaternary alkylammonium compound consisting of one alkyl tail is more effective than the quaternary cation having two alkyl tails in the formation of exfoliated nanocomposites. This is due to the pronounced interaction between the polyamide and organoclay platelets rather than the platelet-platelet. Polyamide is very much polar in nature, and it has strong hydrogen-bonding characteristic, and in the polyamide/organoclay nanocomposites, some hydrogen bonding establishes in the interface of the polyamide and organoclay. A schematic illustration showing the formation of hydrogen bonds in PA6– pristine MMT is shown in Fig. 1.10.

LS platelets have been shown to be very effective reinforcements in epoxy systems. The key process to achieve an exfoliation epoxy/LS nanocomposite structure is to load the clay gallery with hydrophobic onium ions first, and the clay platelets expanded the gallery by diffusing in the epoxide chains [93Mes, 94Lan, 98Mas]. The LS enhances the compressive strength of the glassy matrices under compressive load. The dimensional stability, thermal stability, and solvent resistance of the glassy matrix are improved when the clay nanolayers are reinforced [98Mas]. The organically modified LS clay-based polyurethane nanocomposites were first reported by [98Wan]; they observed a tremendous improvement in tensile strength and modulus even in the intercalated clay dispersion [98Wan]. It has been reported that a little addition of the LS (<10 wt%) in thermoplastic polyurethane matrix can lead to the significant improvement in many properties such as tensile strength and tensile modulus, elongation at break, tear strength, stiffness, flame retardancy, gas barrier property, water vapor permeability, water absorption, ionic conductivity, electrical properties, thermal stability, heat distortion temperature, biodegradability, shape memory behavior, and drug delivery property. All these capabilities enhance the potentiality of this material for a wide variety of significant applications, in automotive, military, aerospace, electronics, food packaging, biotechnology, and biomedical fields. Dan et al. [06Dan] prepared the unmodified and modified (Cloisite 30B, Cloisite 25A, and Cloisite 25A) MMT-based thermoplastic polyurethane nanocomposites by melt compounding method. Cloisite 30B reinforced thermoplastic polyurethane nanocomposites exhibited the highest tensile properties as compared to the other modified clays. Chavarria and Paul [04Cha] have investigated the interaction of the organoclay modifier structures such as long alkyl tails, saturation of the primary tail, the hydroxyl ethyl functional groups, length of the alkyl tail, and thermoplastic polyurethane. The hydroxyl ethyl functional groups containing organoclay produced the best dispersion in the thermoplastic polyurethane matrix with the highest reinforcement, but the organoclay having two alkyl tails produced the poorest result. The thermoset polyurethane/LS nanocomposites analyzed by Wang and Pinnavaia [98Wan] exhibited a unique stress–strain behavior, and the nanocomposites resulted in more strength and toughness in comparison with the pristine polymer.

The dispersion of LS into the nonpolar polyolefin systems proves to be a challenge due to the polarity difference between the organically modified LS and the polyolefin systems. However, to modify the interfacial region between the polyolefin and the LS, the stearyl ammonium exchanged montmorillonite, maleic anhydride-modified polypropylene oligomer, and polypropylene mixture are melt processed to obtain fully exfoliated polypropylene/LS nanocomposites. The hydrolyzed maleic anhydride polypropylene intercalated into the LS, which expands the LS galleries and facilitates the incorporation of base polypropylene chains. Here, the maleic anhydride polypropylene and the modified LS were taken in 3:1 proportion, which is found to be more effective in the fabrication of the hybrid nanocomposites and the hybrid which exhibit improved storage moduli in comparison to the pristine polypropylene. These polypropylene/LS nanocomposites are found to be an ideal material and exhibit enhanced barrier properties [98Has, 97Kat]. The nanocomposites based on polyimide system and LS exhibit excellent barrier properties. Polyimide/LS nanocomposite films are produced from the polymerization of 4, 4′-diaminodiphenyl ether and pyrometallicdianhydride in dimethylacetamide (DMA) solvent along with the LS. However, the degree of dispersion of the LS in the polyimide matrix is very poor, and agglomerates of LS were found in the morphological pictures of the nanocomposites. Irrespective of the degree of dispersion of the LS, polyimide/LS nanocomposites revealed a severalfold reduction in the permeability of the gasses like O_2, H_2O, He, CO_2, etc. [93Yan].

Out of the different techniques that have been employed in order to form polystyrene (PS)/LS nanocomposites, the most practical and promising technique for the preparation of PS/LS nanocomposites is the melt intercalation technique to

Table 1.3 Nitrogen permeabilities of clay/rubber nanocomposites with 20 phr of clay

Materials	Nitrogen permeability (10^{-27} m^2 $Pa^{-1}S^{-1}$)
Pure SBR	7.4
SBR with 20 phr of clay	3.4
Pure natural rubber	13.7
Natural rubber with 20 phr of clay	7.3
Pure nitrile butadiene rubber (NBR)	2.3
Nitrile butadiene rubber with 20 phr of clay	1.2

get the intercalated dispersion of the LS. The organically modified LS were mixed with commercially available PS above T_g of the PS via melt processing. The diffusion of the polystyrene polymer into the LS gallery is a slow process and depends on many factors such as alkylammonium chain length and interactions between the polymer, surfactant, and silicate.

Several rubber/clay nanocomposites, including styrene butadiene rubber (SBR)/LS, natural rubber (NR)/LS, nitrile butadiene rubber (NBR)/LS, and carboxylated acrylonitrile butadiene rubber (CNBR)/LS nanocomposites were prepared by directly co-coagulating the rubber latex and LS aqueous suspension. About 3 % of the aqueous suspension of the LS is mixed into the rubber latex and the SBR nanocomposites prepared by the continuous stirring and coagulating technique. The resulted nanocomposites exhibited substantially higher Shore A hardness, tensile strength, and tear strength as compared to the corresponding conventional rubber composites. The tensile strength of the SBR/LS nanocomposites exhibited is six times higher than that of the conventional SBR/clay composites. The enhanced reinforcement leading to increase in tear resistance, tensile strength, and Shore A hardness is due to the uniform distribution of the LS platelets, orientation of the platelets, and the high aspect ratio of LS. The gas permeability of neat SBR vulcanizates, SBR/LS nanocomposites, and SBR conventional composites has been shown in Table 1.3 (Wu et al., 2005). It has been observed from the table that the nitrogen permeability is reduced with increase in the amount of the LS. The SBR/LS nanocomposites exhibited best gas barrier property. This enhancement in the gas barrier property due to the high aspect ratio of the LS layers and their planner orientation leads to the diffusion distance by creating a much more tortuous path for the diffusion gas.

Blumstein et al. [95Blu] first reported the improvement of the thermal stability of polymer/LS nanocomposites based on poly(methyl methacrylate) (PMMA) and organically modified layered silicate. The thermal stability of the PMMA/LS nanocomposites is remarkably higher than the pristine PMMA, the inorganic LS phase being solely the responsible for the enhancement in the properties. The PMMA phase inserted between the lamellae of montmorillonite clay, which restricted the thermal degradation. The neat polydimethylsiloxane (PDMS) vulcanizates show the thermal stability up to 140 °C, and the thermal stability of the PDMS/LS nanocomposites was quite higher than that of the neat PDMS vulcanizates. This behavior is due to the disordered-delaminated distribution of the LS in the PDMS matrix. The improvement in thermal stability and the restricted decomposition of the polymer nanocomposites are also the major cause for the significant enhancement in barrier property of the polymer nanocomposites. Organically modified LS clays are effective reinforcing filler in the fabrication of polymer/LS nanocomposites. By inserting long-chain surfactants into the hydrophilic galleries of the LS, the interlayer distance increases, and the surface chemistry of the LS is modified. By using the newly developed organophilic LSs, the intercalated and exfoliated nanocomposites are fabricated with wide varieties of applications. The melt blending of the hydrophobic thermoplastic polymer and the organically modified LS with some necessary compatibilizer seems to be very promising for nanocomposite formation.

1.1.6 Effect of Carbon Nanotube on the Performance Properties of Polymer Nanocomposites

The first ever preparation of polymer nanocomposites using MWNT as nanofiller is reported in the literature by Ajayan et al. [93Aja]. Nanocomposites based on CNT and polymer matrices have attracted considerable attention in research and industrial communities due to their versatile application and intrinsic mechanical properties, high aspect ratio (>1000), low density, high surface area, and thermal and electrical properties [02Pot]. CNTs possess very high flexibility, and their properties have been attracted to many active research fields over the last decade for their wide variety of applications. The unique combination of mechanical and electrical properties of individual CNT makes it ideal reinforcing nanofiller in a number of applications. Therefore, the use of CNT as electrical conductive and reinforcing filler for polymers has gained tremendous momentum throughout the world. The prime issues in the preparation of MWNT reinforced polymer nanocomposites is the efficient dispersion of CNTs within the polymer matrix, the assessment of the degree of dispersion, and the alignment control of the CNTs in the matrix because they govern the resulting material properties of the polymer/CNT nanocomposites. However, as far as rubber matrices are concerned, insufficient dispersion (due to high viscosity of the rubber matrix and poor interactions between elastomers and CNTs) of CNTs lead to elastomeric composites with low performance properties (Das et al. [08SDas]). Important aspects to be considered for the preparation of CNT composites in polymer matrix are the bonding between both the phases and good dispersion of the filler in the polymer. However, the CNT aggregation in polymer matrix diminishes its reinforcing effects, and the agglomerations dramatically hamper the mechanical properties of the fabricated nanocomposites. The agglomerations are due to the smaller size of CNTs which makes them curl and twist, and therefore individual CNTs embedded in a polymer only exhibit a fraction of their potential [07Fal1, 10Spi]. The attractive van der Waals forces between the outer planes of neighboring CNTs result in the agglomeration. Therefore, homogeneous distribution and good dispersion of the CNTs have been a potential challenge in polymer composites, which are highly needed for the reinforcement of CNTs, and the excellent properties of CNTs can be fully translated into high strength and stiffness of finished products. Furthermore, the physico-mechanical, electrical, thermal, optical, rheological, and damping properties of the polymer/CNT nanocomposites are greatly affected by the degree of dispersion and types of functionalizations of CNTs. There has been an immense effect to establish the most suitable conditions for the transfer of either load or electrical charge to individual CNTs in the polymer nanocomposite system. Various chemical modification methods have proved to be successful in introducing functional moieties, which contribute to better nanotube dispersion, better interfacial adhesion, and eventually efficient thermodynamic wetting of CNTs in the polymer matrix. The aggregation of CNTs in the polymer nanocomposites results in inferior properties as it prevents efficient stress transfer to individual nanotubes and the stress concentrates over there, which facilitates the formation of micro-crack in the composite systems [10Spi]. Especially, for the better dispersion of CNT in the polymer matrix, some nonionic and ionic surfactants have been used in aqueous and organic medium as reported by Vaisman et al. [06Vas]. In literature, it has been reported that with the incorporation of 1 wt% of CNT in presence of surfactant, the T_g increased from 63 to 88 °C and the elastic modulus increased by 30 % [00gon]. Das et al. [08SDas] prepared the high-performance polymer/CNT nanocomposites using specific ionic liquids, and it acts as a coupling agent between the CNT and polymer chains. For a better dispersion of CNT in the polymer matrix, prior to mixing, it needs sonication in ethanol by using ultrasonic bath for 2 h to break the agglomeration in the CNT phase. Hence, for the better dispersion of CNT in the polymer phase, requisite amount of ionic liquid is added in ethanol during sonication. The ratio of the CNTs to ethanol is 1:30 by weight.

The mechanical properties of the CNT-filled polymer nanocomposites and polymer blend nanocomposites are also improved in comparison to the neat polymer. Das et al. [08SDas] reported the sharp rise in the Young's modulus of the styrene butadiene rubber (SBR) and butadiene rubber (BR) blend with incorporation of ethanol-dispersed CNT. Sanay et al. [08San] prepared natural rubber (NR)/MWNT nanocomposites and observed that the compression set increased with incorporation of MWNT, which is due to the reduction in the elasticity of NR nanocomposites with increase in MWNT loading. The tensile strength and the elongation properties of the NR/MWNT nanocomposites also increased, and the optimum value of tensile strength is obtained at 5 phr of MWNT. The maximum tensile strength and elongation of the nanocomposites are 54.64 % and 14.22 %, respectively, which is due to the well-dispersed MWNT and good interface between the MWNT and NR matrix. However, the tensile strength and elongation at break of the nanocomposites [11Nol] decreased gradually beyond 5phr of MWNT loading which is believed to be caused by the premature starting at the MWNT agglomerations.

1.1.7 Effect of Graphene on the Performance Properties of Polymer Nanocomposites

Graphene is a two-dimensional mono-atomic carbon layer which has emerged as an exotic material used nearly in every field of science and engineering and received worldwide attention due to its exceptional properties such as charge transport, thermal, optical, and mechanical characteristics. In recent progress, it has been observed that the graphene-based materials can have profound impact on electronic and optoelectronic devices, chemical sensors, nanocomposites, and energy storage. In graphene, the mobility of the electron is very high at room temperature, and the electrons in graphene behave like massless relativistic particles, which contribute peculiar property like the Hall effect. Graphene exhibits exceptional thermal conductivity (5000 $Wm^{-1}K^{-1}$), superior mechanical properties with Young's modulus of 1 TPa. Graphene-reinforced polymer nanocomposites have shown tremendous potential applications in various important fields such as electronics, aerospace, automotive, and green energy. The reinforcement offers exceptional improvement in the properties of the polymer nanocomposites.

The methods like solution blending, melt blending, and in situ polymerization techniques are the most commonly used for the preparation of graphene-based polymer nanocomposites. The melt intercalation technique is abundantly used for the manufacturing of thermoplastic composites and nanocomposites in large scales. Graphene-filled polymer nanocomposites such as poly(methyl methacrylate) (PMMA)/graphene, poly (ethylene-2,6-naphthalate)/graphene, polycarbonate/graphene nanocomposites were prepared by this method [09Kim, 11Kul]. Lee et al. [12Lee] prepared polystyrene/graphene nanocomposites by solvent casting technique. Polyaniline (PANI)/graphene oxide nanocomposites have been successfully prepared using in situ polymerization technique [09Wan, 10Mas].

The extra ordinarily high mechanical properties such as high elastic modulus and high tensile strength of graphene sheets have attracted the attention of the frontier researchers. The intrinsic strength and elastic modulus of graphene are 125 GPa and 1.1 TPa, respectively. The polystyrene/graphene nanocomposites exhibited improved mechanical properties than the neat polystyrene matrix, which is attributed to the effective load transfer between the graphene and the polymer matrix [10Pat]. Basically, the improvement in properties of polymer/graphene nanocomposites strongly depends on the interfacial interaction which facilitates the high molecular level dispersion and enhanced interfacial interaction leading to high mechanical properties. The poly vinyl alcohol/graphene nanocomposites exhibited enhanced mechanical properties by 76 % and 62 % in elastic modulus and tensile strength, respectively, with 0.7 wt% of graphene loading [13Rah]. The graphene-reinforced nylon-12 nanocomposites have shown improvement in tensile strength and elongation at break by 35 % and 200 %, respectively with 0.6 wt% of graphene loading [10Xu]. The most fascinating and interesting property of graphene is its high electrical conductivity. Graphene-reinforced insulating polymer matrix generates nanocomposites with greatly enhanced electrical conductivity. The electrical conductivity of the resulted nanocomposites depends on the aggregation of the graphene sheets, functional groups on the graphene sheets, concentration and aspect ratio of the graphene sheets, and its distribution in the polymer matrix. However, graphene oxide is electrically insulating in nature, and the thermal reduction of graphene oxide eliminates the oxygen functional groups and the reduced graphene oxide as suitable nanofiller for the fabrication of polymer nanocomposites having enhanced dielectric properties. Reduced graphene oxide sheets in polymer nanocomposites create conductive paths for the electron just above the percolation threshold. The dielectric properties of reduced graphene oxide reinforced polyurethane, epoxy, polyamide, poly aniline, poly vinyl alcohol, poly carbonate nanocomposites have been studied which reveals that these materials can be used for electromagnetic shielding, photovoltaic devices, sensors and conductive paints, etc. [11Pot]. However, the application of graphene-reinforced polymer nanocomposites is limited due to the poor dispersion of the graphene sheets into individual sheets in the polymer matrix. The functionalized graphene sheets provide better opportunity for uniform dispersion in the polymer matrix for improving the mechanical properties. However, the attachment of the foreign molecules may change the charge transport properties. The polymer/graphene nanocomposites have wide applications in energy storage devices and as antistatic coatings.

1.1.8 Conclusions

The critical challenges which need serious attention are the development of suitable methods for homogeneous dispersion of nanofillers within polymer matrix, because uniform dispersion with exfoliated morphology and the establishment of the interconnected network structures leads to significant improvement in performance properties. Various well-established processing methods such as melt blending, solution intercalation, in situ polymerization, as well as proper modification of nanofillers and polymers have overcome the problems of achieving enhanced material properties, but still there exist enough opportunities and challenges to be attended in order to enhance dispersion of nanofillers and interfacial interaction between nanofillers and polymer for development of high-performance polymer nanocomposites. The preparation, modification, characterization, and properties of different nanofiller-based polymer nanocomposites have been discussed in this chapter.

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Polymer Nanocomposites for Electronics, Dielectrics, and Microwave Applications

2

Bibhu Prasad Sahoo and Deba Kumar Tripathy

2.1 Introduction

Composite materials are the materials made up of two or more physically as well as chemically different constituents and different phases separated by a distinct interface. The constituents have different physical as well as chemical properties and, when they combined judiciously, produce a material with more useful structural and functional properties in comparison to the individual constituents. On the basis of matrix phase, composites can be broadly classified into metal matrix composites, ceramic matrix composites, and polymer matrix composites. Mostly nowadays the polymer matrix composites are used in various sectors instead of neat polymers due to the improved properties of the polymer composites. The most common polymers used for polymer composites are polyester, epoxy, vinyl ester, phenolic, polyimide, polyamide, polypropylene, polyethylene, polyether ether ketone, etc. In the composite system, when the dimension of the filler phase is in nano-size, then the composite is known as nanocomposite. Generally, commodity and specialty polymers are insulators because the atoms in the polymer chains are covalently linked. One of the most convenient methods to form interconnected conductive networks in an insulating polymer matrix is the incorporation of conductive fillers such as metallic powders, flakes, whiskers, and other conductive fillers such as carbon black, graphite, carbon nanotubes, graphene, etc. Among these fillers, CNT and graphene are the best versatile reinforcing filler for the formation of electrically conductive paths in the insulating polymer matrix with a very low level of loading as compared to the conventional fillers. These nanofillers

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exhibit high surface area which impart substantial improvement [06Col5] in physico-mechanical and dielectric properties at low level of loading. The carbon nanofiller-based nanocomposites are increasingly being reviewed as the realistic alternative to the conventional smart composites due to the superior electrical characteristics and higher sensitivity [08Hua1].

2.2 Polymer Nanocomposites and Their Applications

2.2.1 Polymer Nanocomposites for Microwave Applications

Electromagnetic interference (EMI) shielding of radio frequency radiation is a serious concern in the present society due to the wide use of communicating devices in commercial, military, and scientific field. The continuous growth in the field of telecommunication and information technology of various emerging radio frequency systems is used. Many electronic instruments with the high frequency, such as satellite communication, automobile collision prevention radar, accident surveillance of railroad, and millimeter-wave wireless local area network (LAN), have been developed and applied [98Hat7, 95Har8]. The electromagnetic microwaves produced from some electronic devices have adverse effect on the performance of the nearby electronic equipments, and this is known as electromagnetic interference. EMI causes the malfunction to medical apparatus, industry robots, and also harmful to human body [01Das9]. This EMI has adverse effects on electronic equipments such as false operation due to unwanted electromagnetic waves and leakage of information in wireless telecommunications. For the easy operation of these various instruments and to restrict the unwanted interference of various electromagnetic radiation, various absorbing materials with high performance and a large operating frequency band have been developed. Conventionally metals and metal-based composites are used as EMI shielding materials as they exhibit high shielding efficiency due to their good electrical conductivity. However, they are possessing poor chemical resistance, oxidation, corrosion, high density, and difficulty in their processing. In comparison to metal and metal composites, conductive polymer and conductive polymer-based nanocomposites are lightweight, resistant to corrosion, flexible, and excellent processability [05Bry10]. EMI shielding effectiveness (EMISE) of the conductive polymer composites mainly depends on the intrinsic conductivity, dielectric constant, and aspect ratio of the filler. The polymer nanocomposites based on CNT are very promising due their high aspect ratio and special conductivity for excellent absorption of electromagnetic radiation with low level of CNT loading. Generally these nanocomposites contain the dispersed CNTs and absorb the microwaves in the frequency range of 40 MHz–40 GHz. The EMI shielding materials made up of polymer and rubber composites are shown in Fig. 2.1.

Fletcher et al. [10Fle11] reported the noticeable EMI shielding effectiveness, and the excellent dielectric conductivity of the MWNT filled foamed fluorocarbon nanocomposites at a very low level of MWNT loading [91Iij2]. The EMI shielding effectiveness of acrylic elastomer/MWNT nanocomposites has been measured in

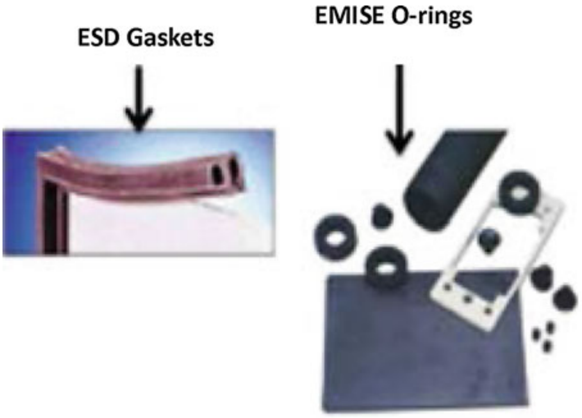


Fig. 2.1 Probable applications of EMI shielding products [10Fle11]

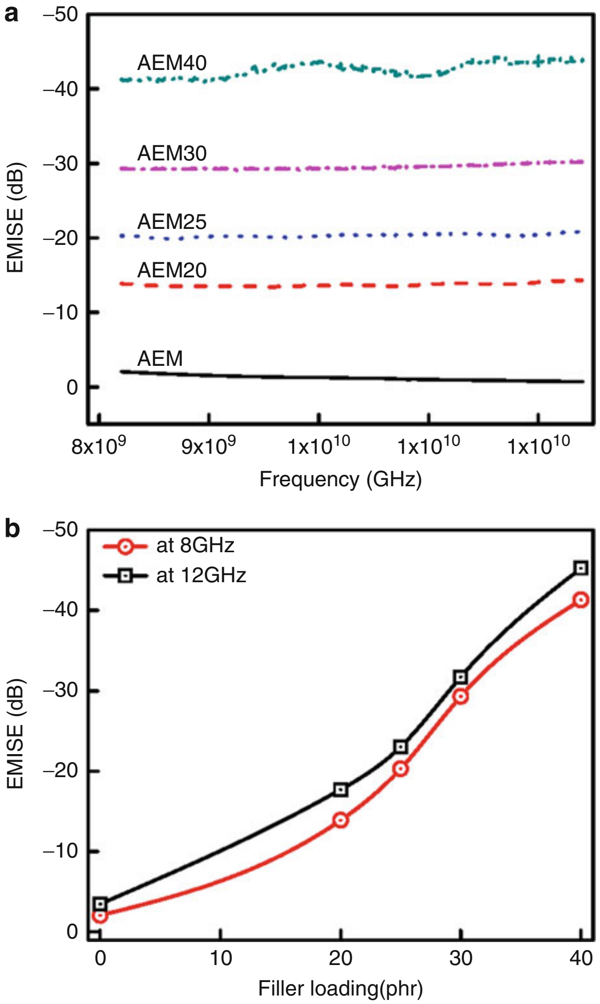
X-band frequency range (Fig. 2.2a and b), and from this figure, it is observed that the EMISE of acrylic elastomer nanocomposite increases with increase in MWNT loading. This may be due to the reflection or multiple reflections of the electromagnetic ray by the acrylic elastomer/MWNT nanocomposites. In literature, it has been reported that for reflection of the electromagnetic radiation, the shield materials should have mobile charge carriers, which increase with increasing the MWNT loading in the acrylic elastomer [01Chu12, 12Mah13]. Hence, the higher the electrical conductivity, the higher is the EMI shielding effectiveness of the shield materials. Other than reflection, EMI shielding effectiveness is also involved in multiple reflections, which refers to the reflection at various surfaces and interfaces in the shield materials. This mechanism requires the presence of large surface area or interface area in the shielding materials, and in the present case, the presence of high-structured MWNT causes the enhancement of EMI shielding effectiveness.

The EMI shielding effectiveness of the functionalized graphene-based polyvinylidene fluoride (PVDF) conductive nanocomposites [09Lia14] has been extensively studied. These nanocomposites exhibited excellent electrical conductivity such as 10^{-5} S/cm with 0.5 wt% of functionalized graphene loading. They reported PVDF with 5 wt% functionalized graphene exhibited approximately 20 dB EMI shielding effectiveness in the X-band frequency region (Fig. 2.3) [01Tho4].

2.2.2 Application of Polymer Nanocomposites for Sensor

In the scientific community, there is a growing interest on the development of graphene-based polymer nanocomposites for sensor application for the unique property of graphene [07Gei15]. The gases like NO_2, NH_3, H_2O, and CO are easily detected by graphene at very low pressure [07Sch16]. Polymers having conjugated double bonds such as PANI, polypyrrol, and polythiophene have been extensively studied for the development of gas sensors. The skeleton of these polymeric chains is

Fig. 2.2 (**a**) EMISE of acrylic elastomer/MWNT nanocomposites. (**b**) EMISE of acrylic elastomer/MWNT with MWNT loading



comprised of conjugated π-bonds, and these π-electrons are very much influenced by the chemical species adsorbed onto their surfaces due to the redox or acid–base type of reaction between the polymer matrix and the chemical species [07Sad17]. The graphene nanosheets provide more active sites for nucleation with PANI like conductive polymer which causes the excellent electron transfer pathways. The graphene-based PANI nanocomposite is used for sensor, and the developed sensor has higher sensitivity toward H_2 gas due to the high aspect ratio of the graphene sheets. The extent of H_2 gas sensing of the sensor made from PANI/graphene nanocomposites is much more than the sensor made from graphene as well as from PANI. A gas sensor based on PANI/graphene nanocomposites is fabricated

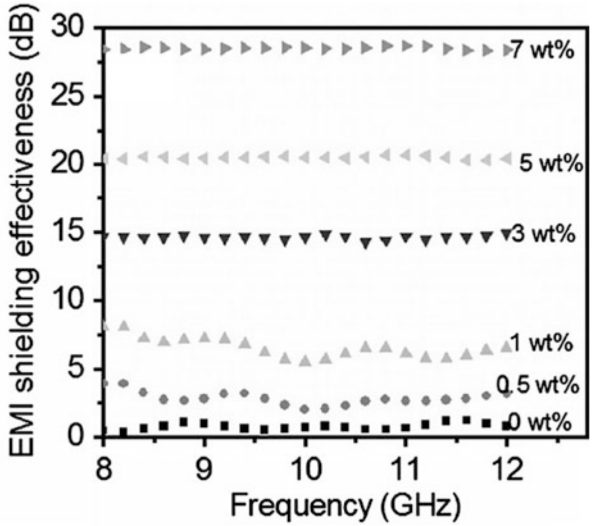


Fig. 2.3 EMISE of graphene/PVDF nanocomposites as a function of frequency in the X-band

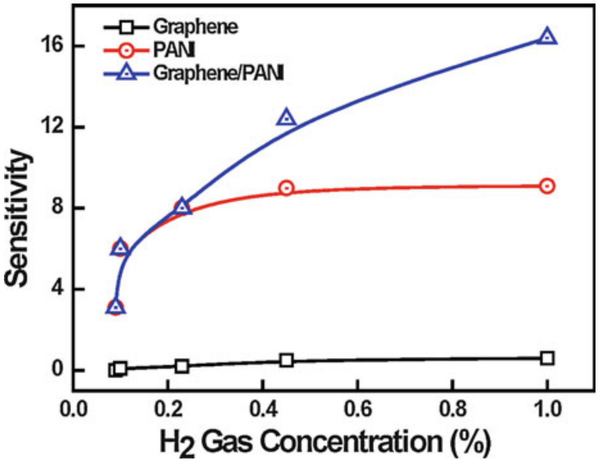
and characterized at different concentration of H_2 gas [10Mas18]. The sensors made from PANI nanofibers are well known for H_2 gas sensing. However, Laith Al-Mashat et al. [10Mas18] compared the extent of H_2 gas sensing of sensor based on graphene, PANI, and PANI/graphene nanocomposites, and they observed that the sensor based on PANI/graphene nanocomposites exhibits highest H_2 gas sensing activity. A comparison plot of H_2 gas sensing under same experimental condition has been shown in Fig. 2.4. The mechanism of H_2 gas sensing in PANI as well as PANI/graphene nanocomposites can be explained on the basis of chemisorptions of H_2 gas molecules at the charged amine nitrogen sites.

The nanomaterials and nanomaterial based on conductive polymer nanocomposites are very much used in biosensors and allow to response of many biological signal transduction technologies. In molecular level microelectronic and sensors, the conductive polymers and conductive polymer nanocomposites have been used as potential systems to check the enzyme activities. In these systems the electrons directly transfer from the enzyme, and the entrapment of enzymes in conductive polymer nanocomposite film provides a controlled method of localizing biological active molecules in defined area on the electrodes [09Raj19].

2.2.3 Application of Polymer Nanocomposites for Capacitor Applications

The super capacitor is an intermediate system between dielectric capacitors and batteries and plays very vital role [08Sim20]. The present scenario is to develop economical electrode materials with a high capacity of charge storage and energy density in the super capacitor. Mainly the materials used for the fabrication of super capacitor are carbon, metal oxides, and conducting polymers. Carbon-based

Fig. 2.4 Sensing activity of PANI and PANI/graphene nanocomposites [10Mas18]



nanomaterials such as CNT and graphene having extraordinarily high surface area and excellent electrical conductivity have been attracted the attention of the scientific community for different applications. These carbon nanomaterials are mostly used as a substitute of metal oxide for the electrode of capacitors. Compared to the CNT, graphene is the most focused carbon nanofiller used for the fabrication of super capacitor due to its extraordinarily high surface area and excellent electrical conductivity [07Dik21]. These encouraging characteristics of graphene made it a new emerging material for wide range of potential applications and have attracted great interests in developing multifunctional graphene nanocomposites with other materials [06Sta22].

Conductive polymers are widely used as energy-storing materials in various electrochemical capacitors due to their large pseudo-capacitances and due to the easy storage of charge during the redox processes. Due to the storage of charge in the molecular chain of conductive polymers in its whole volume, the capacitors based on conductive polymers have much higher specific charge density [01Fra23]. The conductive polymers in their nanoform have special importance in the manufacturing of capacitors due to their remarkably high surface area and small dimension, which facilitates the diffusion of electrolytes in the polymer matrices and exposes more active sites for redox reactions [05Zho24]. Conductive polymers like PANI and polyvinylidene fluoride (PVDF) have been extensively studied and widely applied in various electronic devices nowadays. The conductive polymer- and carbon-based nanofiller nanocomposites are regarded as good alternative candidates for the manufacturing of capacitors. CNT/graphene and conductive polymer-based nanocomposites act as the templates for the electrosynthesis of conductive polymers and enhance the dielectric conductivity as well as the electron transportation of the device [08Pen25]. Therefore, presently these conductive polymers blended with various conductive nanofillers have been applied for the fabrication of chemical sensors, actuators, memory devices, batteries, and super capacitors [10Wu26].

Cuentas-Gallegos et al. [05Cue27] synthesized PANI/polyoxometalate nanocomposites, and the resulted nanocomposites exhibit high specific capacitance than the individual components. Frackowiak et al. [06Fra28] have fabricated three different types of conductive polymer nanocomposites using three different polymers such as polyaniline, polypyrrole, and poly-(3,4-ethylenedioxythiophene) filled with MWNT. They have tested these three nanocomposites as super-capacitor electrode materials. The capacitive nature of these composites increased noticeably in comparison to the unfilled materials, and this is due to the electrostatic attraction between the MWNT and base polymer matrix which is called as pseudo-capacitance. The MWNT plays very vital role as a perfect backbone for energy storage in the capacitor. It has been observed that the conductive polymers in their pure form are mechanically weak and the CNT reinforces the materials and the nanocomposites can withstand the mechanical changes like shrinkage and breaking during long-cycle operation [99Sal3]. They observed the presence of MWNT improves the charge transfer which enables very well the high charging and discharging processes [06Col5]. The capacitance values after the incorporation of MWNT increased from 100 to 330 F g^{-1} with a capacitor voltage from 0.6 to 1.8 V.

2.2.4 Dielectric Properties of Polymer/Carbon Nanofiller Nanocomposites

Electrical properties of polymers are their responses to an external electric field, and polymers cover an extremely diverse range of molecular phenomenon in the electric field. CNTs have clearly demonstrated their capability as nanofiller in diverse multifunctional polymer nanocomposites. Polymer nanocomposites based on carbon nanofiller have emerged as advanced multifunctional materials for their exceptional dielectric properties, which create the key interests to develop conductive polymer nanocomposites preferably at low concentration of carbon nanofiller loading. Polymer/CNT nanocomposites exhibit percolation behavior due to the formation of interconnected conductive networks, which results in a dramatic increase in electrical conductivity. These polymer nanocomposites have numerous applications in antistatic devices, conductive coatings, electrostatic painting, and piezoresistive materials for their excellent dielectric properties. Thus, the exploration of the dielectric properties of the polymer/carbon nanofiller nanocomposites is an essential issue for frontier researcher and developments.

Park et al. [12Par29] have reported the nanocomposites based on PMMA and MWNT that exhibited significant enhancement in the AC conductivity (σ_{ac}), and $\approx$ 3000 S/m σ_{ac} was found at 0.4 wt% of MWNT loading prepared by solution mixing. Polycarbonate (PC) nanocomposites based with 15 wt% of MWNT exhibited 16 times more σ_{ac} than the unfilled PC [07Pot30]. Koerner et al. [05Koe31] have reported that the PU/MWNT nanocomposites prepared by solution casting method exhibited 2000 S/m σ_{ac} at 27 wt% of MWNT content, and the PANI nanocomposites based on 15 wt% of MWNT loading exhibited the same σ_{ac} value. Polyphenylene sulfide (PPS)-based MWNT nanocomposites containing 5.4 wt% of

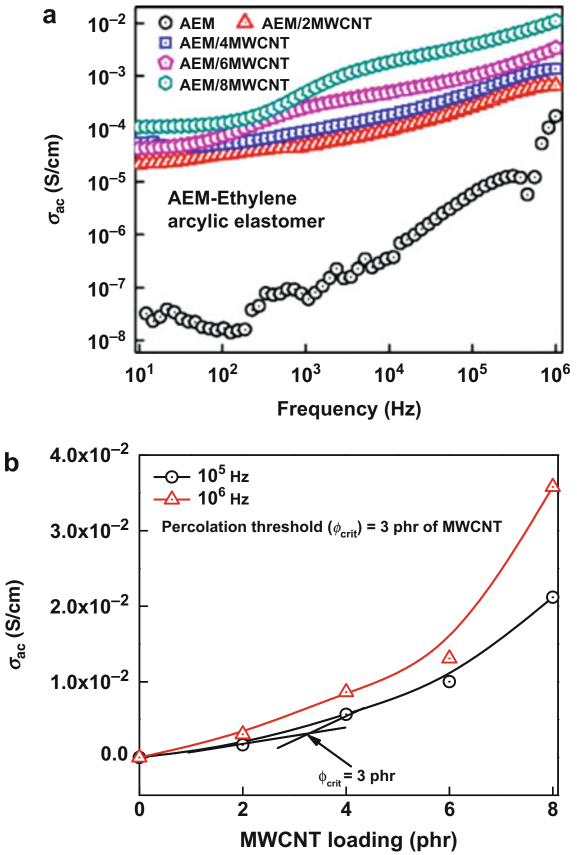


Fig. 2.5 (**a**) The variation of σ_{ac} of acrylic elastomer/MWNT as a function of frequency. (**b**) The variation of σ_{ac} of elastomer/MWNT as a function of MWNT

MWNT exhibited σ_{ac} of 1000 S/m at relatively low percolation threshold (0.396 wt%) [11Nol32]. Zhu et al. [06Zhu33] reported the gradual increase in σ_{ac} with increase in MWNT loading in the polyimide/MWNT nanocomposites and observed a sharp increase in the σ_{ac} within 7 to 10 wt% MWNT loading. This phenomenon was due to the formation of percolative networks at this loading level of MWNT. The percolation threshold is characterized by sharply jumps up in the electrical conductivity of the composites by several orders of magnitudes due to the formation of continuous three-dimensional conductive network of the conductive fillers within the insulating polymer matrix.

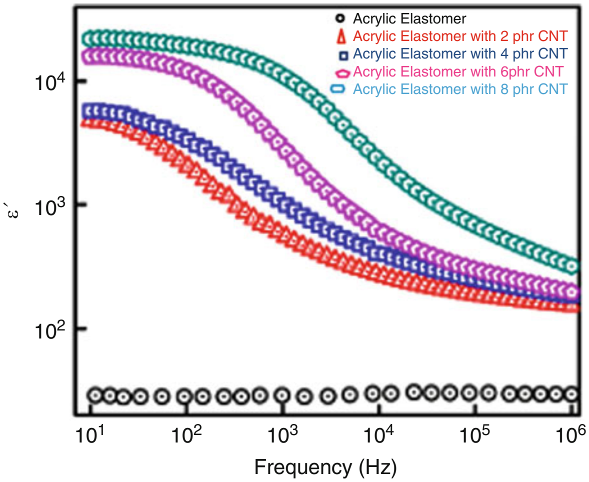
The variation of σ_{ac} with frequency for acrylic elastomer nanocomposites with different concentration of MWNT has been shown in Fig. 2.5a, and it is observed that irrespective of the MWNT loading, the σ_{ac} of the nanocomposites predominantly increases with increasing the frequency of applied electric field. This increase in σ_{ac} with frequency can be explained in terms of hopping and tunneling mechanism. A monotonous increase in σ_{ac} with MWNT loading has been observed from Fig. 2.5b. The dramatic increase of σ_{ac} of the acrylic elastomer nanocomposites by adding MWNT is due to the formation of interconnected nanotube networks and transformation of the insulating polymer matrix to conductive nanocomposites at a minimum concentration of MWNT, which is known as percolation threshold. The percolation threshold is generally determined by plotting the electrical conductivity as a function of the conductive filler loading. Electrical conductivities for conductive nanocomposites are known to depend on microstructures of the conductive fillers such as filler particle geometry, aspect ratio, dispersion, alignment, and filler–filler interactions [05Son34]. The MWNTs having large aspect ratio are obviously more effective in the enhancement of electrical conductivity of the acrylic elastomer nanocomposites due to their long lengths that could achieve easy connection points between themselves [07Yan35].

Dielectric constant or relative permittivity (ε') reflects the ability of materials to store electrical energy. Imposition of an electric field upon a polymer causes the redistribution of charges in the polymer and polarization of the charge particles or the molecules along the direction of applied electric field, and from the extent of polarization, the static relative permittivity or dielectric constant (ε') can be calculated for that particular polymeric system. The materials showing greater polarizability of the molecules exhibit higher ε' value. The polarizability of polymeric systems involves electronic polarization (the applied electric field causes a displacement of electrons relative to the nucleus) and atomic polarization (the applied electric field causes the displacement of the atomic nuclei relative to one another). However, with the systems being composed of polar molecules, the polarization involves the orientation polarization in which the applied electric field causes a net orientation of the dipoles parallel to the field.

Generally, the ε' of polymers is very less, and to increase the ε', they need to be compounded or blended with the conductive fillers for various applications. The effect of conductive fillers like conductive carbon black and carbon nanotubes on the dielectric properties of polymers is very instructive. In literature, the enhancement of ε' due to the incorporation of conductive filler is reported by many researchers. However, this effect is more prominent at lower frequency of applied electric field, and ε' decreases with increase in frequency of the electric field [10Nan36]. In case of very low CNT-loaded (1 phr) rubber vulcanizates, there is no appreciable enhancement in ε', and like unfilled rubber, ε' is independent on frequency of electric field. However, with increasing CNT loading, this behavior is changed. At low frequency, the ε' significantly increases with the amount of CNT loading, but at a particular frequency, the relaxation phenomena occur and the ε' decreases drastically with frequency. However, with increasing the CNT loading, the relaxation transition is shifted toward higher-frequency region.

The frequency dependency of the ε' of the acrylic elastomer/MWNT nanocomposites is shown in Fig. 2.6. From Fig. 2.6, it is observed that the unfilled acrylic elastomer vulcanizate exhibits low ε' value and behaves almost independent of the frequency of the applied electric field. However, with increasing the incorporation of MWNT, the ε' increases and the increase is more significant at lower frequency. The higher value of ε' could be realized through interfacial polarization mechanism [06Li37] and proper orientation of dipoles formed by the MWNT phase

Fig. 2.6 The variation of ε' of AEM/MWNT with respect to frequency



in the acrylic elastomer matrix along the direction of applied electric field. In the present case, the acrylic elastomer nanocomposites containing 8 phr of MWNT exhibit highest ε' value. It has also been observed from the figure that ε' continuously decreases with increase in frequency and reaches a constant value at around 10^5 Hz. The drastic reduction in ε' with increasing frequency is due to the relaxation process of the dipoles. But at a particular frequency, the relaxation phenomenon occurs resulting in a drastic reduction of the ε' with increasing frequency. At higher frequency of applied field, the dipoles are difficult to orient themselves along the direction of external electric field due to the periodic alternation of the applied electric field.

2.3 Conclusions

Carbon nanomaterials play an important role for the development of multifunctional polymer nanocomposites for various applications. Their excellent conductive nature supports for the formation of interlinked conductive networks in the insulated polymer matrix. The electromagnetic radiation can easily shielded by the conductive nanocomposites for the dielectric nature of the resulted nanocomposites. The conductive polymer nanocomposites based on PANI are used in sensor for sensing of gages like hydrogen and nitrogen, due to their low resistance and very good dielectric permittivity.

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Polymer Nanocomposites for Structure and Construction Applications

3

Moumita Naskar

3.1 Introduction

Composite is a material made by combining two or more constituent materials – often ones that have very different properties, when combined, produce a material with completely different characteristics from the individual components. However, within the composite, constituent materials do not dissolve or blend into each other. The first man-made composite is straw and mud combination to form bricks or walls for building construction [00Lop]. Thousand years ago in ancient Greece, metals were used to reinforce the tension face of concrete beams. Since then the invention of new class of composite materials for structure and construction application is gradually gaining importance to the civil engineers, both for the rehabilitation of existing structures and for the construction of new facilities. So, the glorious entry of polymers in structure and construction application was obvious with its discovery, and first polymer composites were developed during the 1940s for military and aerospace applications. After that polymer composites are used in numerous civil applications, and the most visible application is the pave of roadways in the form of either steel and aggregate reinforced Portland cement or asphalt concrete. The construction sector is the large consumer of polymer composites, and about 30 % of all polymers produced each year are used in the civil engineering and building industries [90Hol].

Polymer matrix-based nanocomposites have generated a significant amount of attention in civil infrastructure application. This area developed with the recognition that nanoscale fillers could yield significant mechanical property advantages as a modification of polymeric systems [08Nju]. The significance of the nanometric size is not only the small scale, but the materials obtain huge specific surface areas at this level, and this huge surface area offers the unique properties of the nanofillers such

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as mechanical properties and low concentrations along with the advanced characterization, and simulation techniques can bring abrupt changes in the polymer nanocomposites [14Dor]. Among the polymer nanocomposites, fiber-reinforced polymer (FRP) composites are most common and effective for this particular purpose. FRP composites are the combination of polymeric resins, which act as matrices or binders, with strong and stiff fiber assemblies which act as the reinforcing phase [05Tuk], and the combination of the matrix phase with a reinforcing phase produces a new material system with unique properties. Its manufacturing process is also “greener” than concrete and steel, as manufacturing of concrete and steel requires much more energy and water than composite manufacturing. The use of FRP composites can improve stiffness/strength, durability, whole-life cost benefit, environmental impact, and innovation. FRPs provide nonmagnetic and noncorrosive products with higher strength to weight ratios, and it could be applicable for highly seismic zone [97Ham]. So, the use of FRPs has been increasingly considered for structural load-bearing applications by the construction industry and has established themselves as a viable selection for rehabilitation and retrofit of existing civil structures. Depending on the application environment, load performance, and durability requirements, potential applications of FRP composites have been found mainly in bridge decks and superstructures, highways, corrosion-resistant reinforcing bars, structures with longer spans resulting in reduced self weight, seismic column, utility poles, and towers, strengthening and wrapping of in-service structures. Therefore, selection of the polymer matrix and reinforcing components depends on the environment, performance, and end user requirements intended use of the product. Polymer nanocomposites are also used to improve the properties of asphalt, an important construction material for pavement.

3.2 Fiber-Reinforced Polymer

3.2.1 Constituents of Fiber-Reinforced Polymer

3.2.1.1 Polymer Matrix

Polymer matrix plays an important role in FRP. Polymer matrix binds the fibers together, transferring the force between the individual fibers. It disperses the fibers within the composite and protects them from mechanical and environmental damage, delamination, water absorption, chemical attack, high-temperature creep, etc. that eventually cause failure of the composite. And finally, the matrix part can only give shapes to the FRP component. Matrices are made of resins selected for civil infrastructure on the basis of the application, environment, and type of processing. Polymeric resins exhibit an extensive variation of mechanical and physical properties over a wide cost range. A polymer matrix can be made of by both thermoplastic polymer and thermoset polymer [05Tuk]. The basic requirements for a matrix material are it must have lower modulus and greater elongation at break than the fibers it is holding, so that the fibers can carry maximum load. Type of matrix

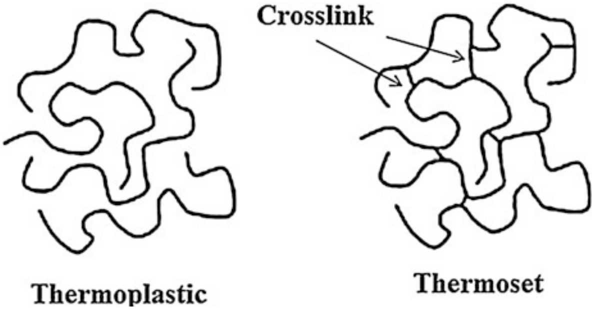


Fig. 3.1 Thermoplastic and thermoset polymers

material and its compatibility with the fibers also significantly affect the properties of the composite.

Thermoplastic resins can be softened repeatedly on application of thermal energy. Thermoplastic polymers consist of linear molecules which are not interlinked as shown in Fig. 3.1. The intramolecular force in the chain is extremely strong, but the intermolecular forces of attraction between the adjacent chains are weak. Commonly used thermoplastics are nylon, polyetheretherketine (PEEK), and polyphenylene sulfide (PPS). The long, disconnected polymer chains melt to a viscous liquid at the high processing temperature and after forming are cooled to an amorphous, semicrystalline, or crystalline solid. The degree of crystallinity has a strong effect on the final matrix properties. Thermoplastic resins provide excellent damage tolerance property due to its high-impact strength and fracture resistance [93Mal]. Thermoplastic resins also provide higher strains to failure, which gives better resistance to micro-cracking in the matrix of a composite and a minimum stiffness to prevent buckling of the fibers. Moreover, thermoplastic resins can be recyclable, and fabrication time is less and easy to handle, but its creep resistance and thermal stability are poor. Mainly thermoset resin-based FRPs are used in civil infrastructures. In thermosetting, polymer chains are cross-linked to each other so that the polymer cannot flow or soften by heating as shown in Fig. 3.1. Thermoset resins give better mechanical properties, chemical and thermal stability, and high rigidity and dimensional stability. Thermosets achieve good wet-out between fibers and resins, which results in better creep resistance than thermoplastics. Thermosets are usually brittle in nature. However, stress relaxation behavior is poor in thermoset resin which lowers its strain to failure. They are usually made from liquid or semisolid precursors and manufacture by polycondensation, polymerization, or curing to get tightly bound three-dimensional, hard, and solid polymer. Unlike thermoplastic polymers, once thermosetting polymers are cured, they cannot be reheated and reformed. Common resin materials include polyester, epoxy, polyurethane, vinyl ester, phenol, etc. [03Fib].

Currently polyesters are the most widely used matrix of FRP in construction application. Polyesters are produced by the condensation polymerization of dicarboxylic acids and difunctional alcohols (glycols) [12Sal]. Depending upon the structures of their basic building blocks, unsaturated polyesters are divided into orthopolyester, isopolyester, and vinyl ester. Besides of their good mechanical,

Table 3.1 Properties of unfilled polymer matrix [02Maz]

Resin	Density g/cm^3	Tensile modulus GPa (10^6 psi)	Tensile strength GPa (10^3 psi)
Epoxy	1.2–1.4	2.5–5.0	50–110
Phenolic	1.2–1.4	2.7–4.1	35–60
Polyester	1.1–1.4	1.6–4.1	35–95
Nylon	1.1	1.3–3.5	55–90
PEEK	1.3–1.35	3.5–4.4	100
Polycarbonate	1.2	2.1–3.5	55–70
Acetal	1.4	3.5	70

chemical, electrical properties, easy processing and relatively low cost make them popular throughout the world [08Nju]. In composite structure isopolyester increases impact resistance, provides greater flexibility and thermal stability, and increases resistance to corrosion than orthopolyester. And vinyl ester has even better impact and corrosion-resistant, superior fatigue, and thermal properties.

Epoxies are mainly used for high-performance composites with superior mechanical properties, resistance to corrosive liquids and environments, superior electrical properties, good performance at elevated temperatures, good adhesion to a substrate, and low shrinkage during the cure. A wide variety of epoxy resin formulations are available providing a broad spectrum of properties.

Phenolics are a class of resins commonly based on phenol and formaldehyde. Phenol is used when there are requirements for high fire resistance, low smoke generation, and flame retardation when subjected to fire. They also have many desirable performance qualities including high-temperature resistance, creep resistance, excellent thermal insulation, sound damping properties, and corrosion resistance.

Polyurethane is prepared by an exothermic reaction of polyisocyanates with polyols. Polyurethane has good impact resistance and rapid curing of the resin, and the resin bonds nicely to a variety of different surface but costs about twice as much as polyester-based composites (Table 3.1).

3.2.1.2 Fibers

The primary function of fibers is to carry load along the length of the fiber to provide strength and stiffness in one direction, thermal stability, and other structural properties to the FRP. Reinforcement effects can be oriented to provide tailored properties in the direction of the loads imparted on the end product. A fiber is a material made into a long filament that can be both amorphous and crystalline and usually has a diameter up to 15 μm [89Fel]. The aspect ratio, i.e., the length-to-diameter ratio, can be ranging from thousand to infinity in continuous fibers. There are three types of fibers dominating civil engineering industry: carbon, glass, and aramid fibers [11Pot].

Carbon Fiber

Carbon fibers are a type of high-performance fiber available for civil engineering application. Carbon fibers are hollow cylinders with diameters typically in the range

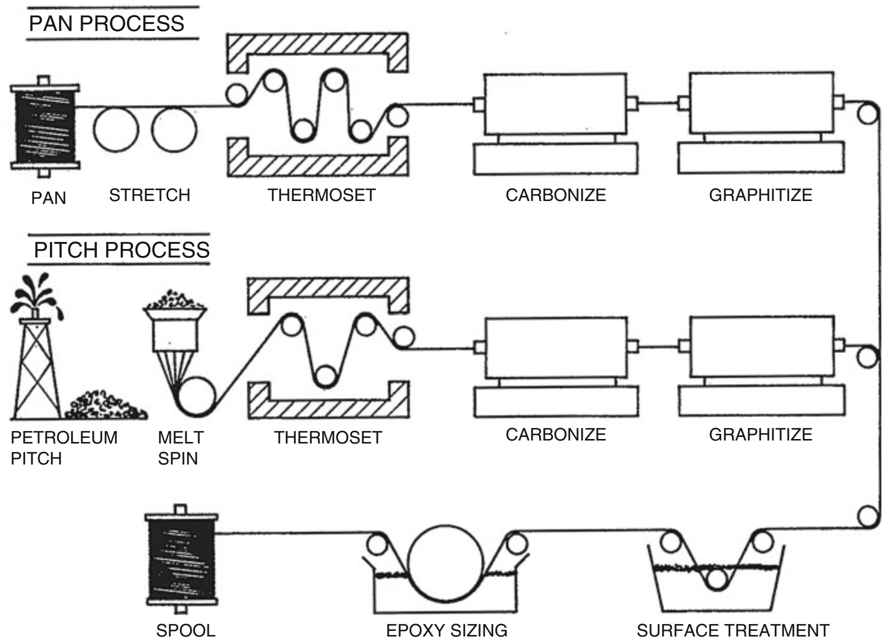


Fig. 3.2 Schematic of PAN and pitch-based carbon fiber manufacturing procedure

of 50–500 nm and lengths of a few tens of microns giving high aspect ratios (length/diameter >100) with parallel and homogeneous alignment of nanoscopic graphene layers along the axis. Polyacrylonitrile (PAN) and mesophase pitch (MP) are the two most important carbon fiber precursors. Carbon fibers are manufactured by controlled pyrolysis and crystallization followed by carbonization and graphitization of these organic precursors at temperature range of 1500–2000 °C in inert atmosphere, and the schematic diagram is presented in Fig. 3.2. In this process, carbon crystallites are produced and oriented along the fiber length [88Bun, 09Xia]. Carbon and graphite are both prepared in similar way. Only extended time and temperature processing is required to form this ordered graphite fibers, and these are based on graphene (hexagonal) layer networks present in carbon. When the graphene layers or planes are stacked in three-dimensional orders, graphite formed. The structure of carbon fibers is similar to that of graphite, consisting of carbon atom layers (graphene sheets) arranged in a regular hexagonal pattern, as shown in Fig. 3.3 [67Joh].

Carbon fibers have excellent elastic modulus, fatigue strength, low densities, and excellent creep resistance [11Jai]. Carbon fibers are very stiff and strong, 3 to 10 times stiffer than glass fibers. Carbon fiber-reinforced polymers have more service life than aramid and glass fibers. Carbon fiber composites are more brittle (less strain at break) than glass or aramid. Carbon fibers can cause galvanic corrosion when used next to metals. Their disadvantages include inherent anisotropy (reduced

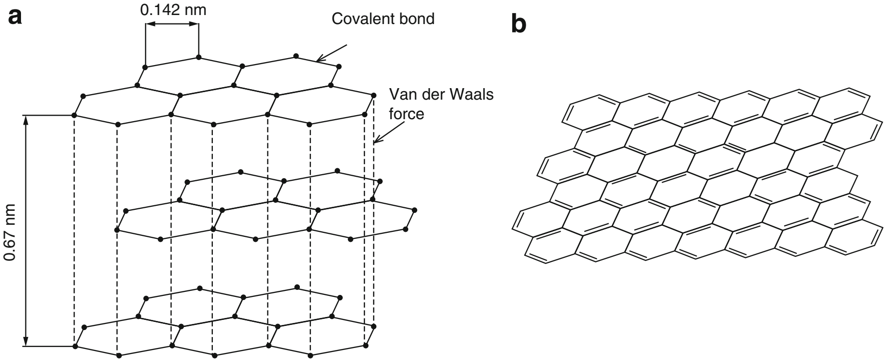


Fig. 3.3 Chemical structure of carbon fiber

radial strength), poor thermal and chemical stabilities in the presence of oxidizing agents, electrical conductivities, galvanic corrosion when used with metals, and costs. Carbon fiber is gray or black in color and is available as dry fabric and prepreg form.

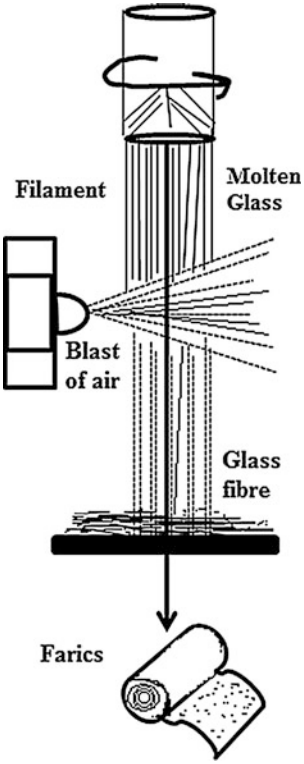
Glass Fibers

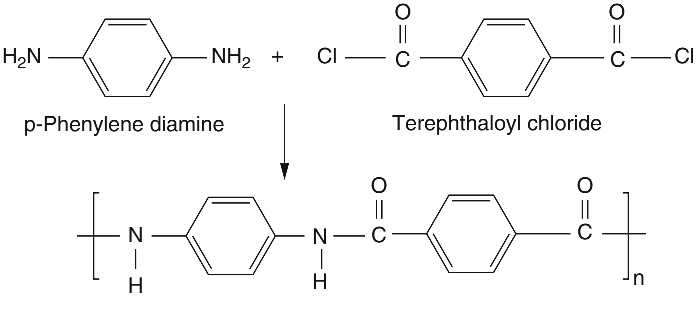
Glass fibers are manufactured by continuously drawing molten glass through small holes in electrically heated platinum bushings at high speeds, approaching 200 miles per hour as shown in Fig. 3.4. And immediately the filaments are cooled from a liquid state at about 1200 °C to room temperature in approximately 10^{-5} s. After that they are bundled together and bonded to one another by a lubricant or “size” to reduce the abrasive effect of the filaments rubbing against one another, damage to fibers during mechanical handling. Sizing also improves wettability of the fiber surface with the matrix and creates stronger bond between them [93Mal]. There are four types of glass fibers, A, E, C, and AR glass fibers, available in five forms such as chopped fibers, chopped strands, chopped strand mats, woven fabrics, and surface tissue to reinforce the matrix material. “E” glass fiber which is basically an alumino-borosilicate glass is most widely in the construction industry especially with polyester and epoxy resins. “AR” glass fiber has been developed for reinforcing cements, mortars, and concrete due to the presence of increased amount of zircon oxide, and that gives highly resistant to alkali attack. The disadvantages of glass fibers are a relatively low modulus, the low humidity resistance, and the stress rupture on long-term use.

Aramid Fiber

Aromatic polyamide fibers, commonly known as aramid fibers, are prepared by the polycondensation reaction between appropriate diamines (*m* or *p*-phenylene diamine) and acid chlorides (isophthaloyl or terephthaloyl chloride) followed by the wet spinning from a solution of concentrated sulfuric acid. The procedure is depicted in Fig. 3.5. It has highest strength to weight ratio with the added advantage

Fig. 3.4 Schematic diagram of manufacturing of glass fiber





Chemical structure of armid

Fig. 3.5 Chemical structure of aramid fiber

of toughness or damage/impact resistance. Aramid fibers are insulators of both electricity and heat. They are resistant to organic solvents, fuels, and lubricants. Aramid composites are high temperature and flame resistant but not as good in compressive strength as glass or carbon composites. Strong amide linkage (−CO-NH-), aromatic rings, hydrogen bonds, and chain rigidity in aramid fibers

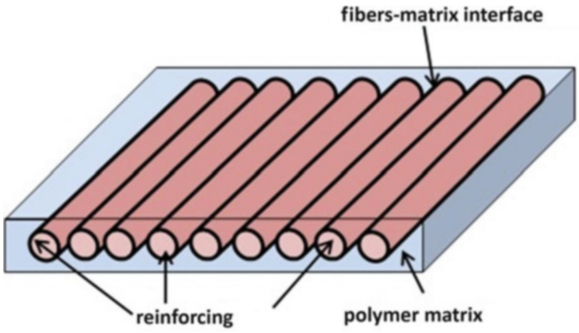


Fig. 3.6 Schematic representation of polymer–fiber interaction

are responsible for all these properties [02Wu]. But aramid fibers are sensitive to moisture, acids, salts, and ultraviolet radiation. There are two forms of fibers, rovings and fabrics, mainly used in civil infrastructure to obtain maximum reinforcement. In roving a bundle of fibers having low twist reinforce the polymer composite in a single dimension, where in order to strengthen the composite in more than one direction of reinforcement, fabric forms are used.

3.2.2 Reinforcement Mechanism

The matrix part of the composite has low strength and low modulus, and the fiber is the high-strength and higher modulus component. Under stress the matrix flows and transfers the load to the fiber which finally results in a high-strength and high modulus composite. In a composite fiber is the primary phase that bears the load due to its high mechanical properties and aspect ratio. But this primary phase must be well dispersed and bonded properly with the matrix, the secondary phase. Hence, the fiber–matrix interface plays the most important role in reinforcement mechanism [01Hol]. The interface provides adequate chemical and physical bonding and stability between the primary and secondary phases by coupling between these two phases. It is a dominant factor in the resistance of the composite to corrosive environments. The interface area is small as per Fig. 3.6, but it has significant role in controlling the overall stress–strain performance of the composite.

This interface will allow stresses to be dispersed through the matrix and then to be transferred to the reinforcement. It also has a vital role in the failure of the polymeric composites and fracture toughness also. Mainly matrix controls the interfacial phenomena, serves as a medium of load transfer to the fabric, and separates the individual fibers, thereby preventing brittle crack. The mechanical performance and structural integrity of the FRP composites depend on the effectiveness of the bond between polymer and fiber. So the selectivity of the resin phase and its consequent fiber is of significant importance. This interfacial interaction can be improved by wetting the reinforcement with the matrix in the molten or low viscosity state [05Hig].

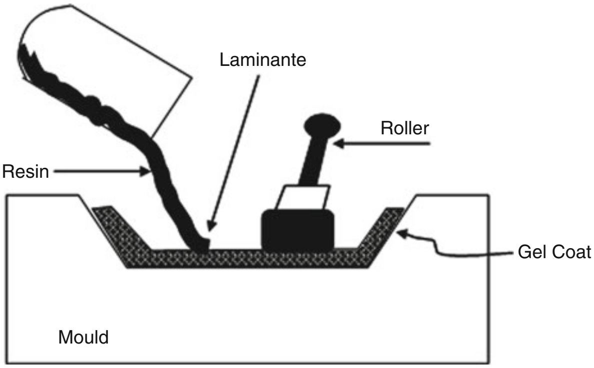


Fig. 3.7 Schematic representation of hand layup process [14Pla]

3.2.3 Composite Fabrication

The fabrication and shaping of composites into finished products often combine the formation of the material itself during the fabrication process. While choosing the technology of manufacturing fiber-reinforced composite for civil infrastructure, number of factors should be considered including final properties of the composite, mechanical compatibility between the reinforcement and the matrix, accuracy of dimensions, quality of the surface, coefficient of thermal expansion, etc. Fabrication of composite materials is accomplished by a wide variety of techniques but few methods related to civil engineering, including hand layup, spray-up, pultrusion, filament winding, and resin transfer molding [14Com].

3.2.3.1 Hand Layup

The oldest, the simplest, and the most commonly used method for the manufacture of both small and large reinforced products is the hand layup technique. In this manual processes, liquid resin is applied to the mold, and fiber reinforcement is placed manually on top as shown in Fig. 3.7. The fibers on this exposed surface must be protected with a resin-rich coating known as a gel coat, and a metal laminating roller is used to impregnate the fiber with resin and remove any trapped air. Several layers of resin and fiber are then applied until the composite attains desired thickness. But in this technique, inconsistency in quality of produced parts, low fiber volume fraction, and environmental and health hazards are concerned.

3.2.3.2 Spray-Up

Figure 3.8 shows the preparatory stages of spray-up process which are similar to those for hand layup, but the actual technique is much faster and less expensive. In this process, a spray gun is used to apply resin and chopped reinforcements to the mold. During the spray-up preparation, glass fiber roving is fed continuously through a chopping unit, and the resulting chopped strands are projected onto the mold together with a resin jet. The glass fiber resin matrix is then merged with

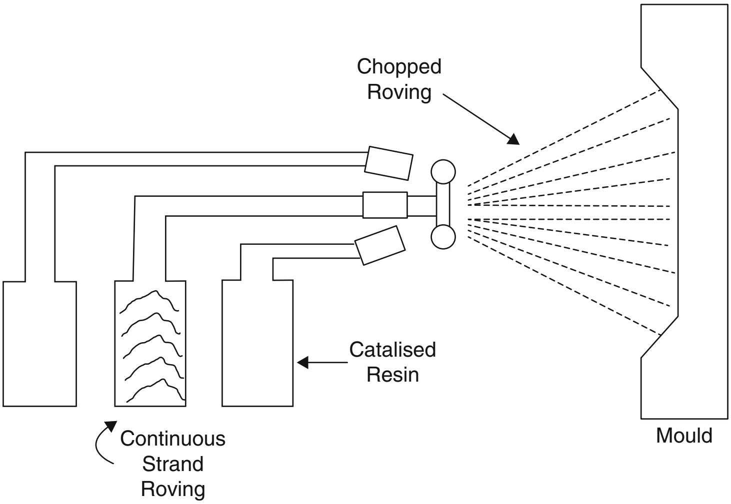


Fig. 3.8 Schematic representation of spray-up process [14Pla]

rollers. But in this process, controlling of the fiber volume fraction and thickness is difficult, and therefore dimensional accuracy hampers.

3.2.3.3 Pultrusion

It is an automated manufacturing process of composites to continuous and constant cross-sectional shape. In this technique, fiber bundles and slit fabrics are pulled from the die through a wet bath of resin and formed into the rough part shape. At this stage appropriate dies can be used to get various types of profiles such as rods, tubes, etc. After that excess of matrix is picked up, and the saturated fiber is extruded from a heated closed die curing while being continuously pulled through die. To cure the formed composite, it is held tightly between rubber blocks and pulled through the die at a predetermined speed and then cut to the desired length by a cutoff wheel. When the fiber is pulled into the processing equipment, the matrix is added by injection. The injection method is an entirely enclosed process in which minimum evaporation of solvents is found. Pultrusion by injection is helpful to control and check the reinforcement. The properties of the finished product depend on the pulling speed and degree of impregnation of the fibers.

3.2.3.4 Filament Winding

Filament winding is a technique in which fiber bundles are pulled through a wet bath of resin and wound over a rotating mandrel at the desired angle to produce high-performance hollow symmetrical products such as pipes, tanks, pressure vessels, and load-bearing tubes. High-speed precise laydown of continuous fiber in predetermined patterns is the basis of the filament winding method. Therefore, starting materials for this process are continuous glass, carbon, or aramid fibers, and liquid thermoset epoxy, polyester, and vinyl ester resins are used in this process.

The composite unit is then removed from the mandrel and cured by being placed in an oven enclosure at 60 °C for 8 h. It is a comparatively low-cost process.

3.2.3.5 Resin Transfer Molding

Resin transfer molding (RTM) is a low-cost process in which large, integrated, high-performance products are fabricated. In this process dry reinforced material has been cut and shaped into a preformed piece which is generally called “perform.” These preforms are then more easily laid into the prepared mold cavity. A second mold tool is then clamped over the first, and a pressurized mixture of thermoset resin, catalyst, color, filler, etc. is injected into the cavity using dispensing equipment to form structural parts. Once all the reinforced material is wet out, the resin inlets are closed, and the laminate is allowed to cure. The mold can also be heated to accelerate the cure of the resin and so reduce cycle times.

3.2.4 Properties of Carbon Fiber-Reinforced Composites

Carbon fibers are a type of high-performance fiber available for civil engineering application. Carbon fiber consists of very thin strands of the element carbon. Carbon fibers have high tensile strength and are very strong for their size. In fact, carbon fiber might be the strongest material. Carbon fibers have high elastic modulus and fatigue strength. They are highly chemically resistant and have high-temperature tolerance with low thermal expansion and corrosion resistance. These improve the service life of carbon fiber-reinforced composites.

Advantages of carbon fiber used for construction application

3.2.4.1 High Specific Strength

Carbon fiber has high strength to weight ratio, i.e., high specific strength. Carbon fiber is strong and light and due to these, it has a favorable strength/weight ratio. So, the composite usually provides these properties at substantially less weight than metals: their specific strength and modulus per unit weight is almost five times that of steel or aluminum.

3.2.4.2 Rigidity

Deflection of carbon fiber under stress is very less which can be measured by its Young’s modulus.

3.2.4.3 Corrosion Resistant

Carbon fiber has high corrosion resistance. Carbon fiber does not easily deteriorate under UV radiation so it can protect the composite from sunlight.

3.2.4.4 Chemical Stability

Carbon fiber has good chemical resistance. Carbon fibers are made of carbon where carbon content is more than 95 %. Long carbon polymer chain is present in carbon fiber and does not have any free bonds or sites to react. Hence, most of the chemicals in low concentration have no effect on the fibers. This makes it possible to use carbon fiber in concrete structures, which works in aggressive environment conditions.

3.2.4.5 Fatigue Resistance

Many civil construction experiences fatigue loading, in which the internal stresses vary with time. These fatigue stresses can lead to failure, even when the maximum stress is much less than the failure strength of the material. Carbon fiber has good fatigue resistance, and failure is unlikely to be a problem when cyclic stresses coincide with the fiber orientation. The orientation of the fibers and the different fiber layer orientation have a significant influence on fatigue.

3.2.4.6 Tensile Strength

Carbon fiber has good tensile strength, but its brittleness does not always fail at the same stress level due to both surface and internal flaws and fail at small strains. Composites can be made anisotropic and have different tensile properties in different directions, and this can be used to design a more efficient structure.

3.2.4.7 Fire Resistance/Nonflammable

Depending upon the manufacturing process and the precursor material, carbon fiber can be quite soft and can be made into or more often integrated into protective clothing for firefighting. Nickel-coated fiber is an example. Because carbon fiber is also chemically very inert, it can be used where there is fire combined with corrosive agents. Carbon fiber blanket is used as welding protection.

3.2.4.8 Low Coefficient of Thermal Expansion

This is a measure of how much a material expands and contracts when the temperature goes up or down, and this is important. Thermal expansion is an important property for extraordinary cases, as it determines saving of shape and rigidity under high temperatures. Also this property is very important for long-span structures. Carbon fiber can have a broad range of coefficient of thermal expansion -1 to 8+, depending on the starting source and manufacturing process. Low coefficient of thermal expansion makes carbon fiber suitable for applications where small movements can be critical.

3.2.5 Disadvantages of Carbon Fiber Used for Construction Application

- Cost of carbon fiber is relatively high.
- Carbon fiber is brittle in nature and carbon fiber-reinforced composite has low strain to failure.
- Compressive strength of the composite is lower, and larger diameter fiber does not give improved compression properties. It also has poor impact strength.

- Carbon fiber is electrically conductive. This feature can be useful and be a nuisance. Accumulated carbon fiber dust can cause sparks and thereby short circuits in electrical appliances and equipment. Careful preparation and installation of composite can reduce this problem.
- Thermal conductivity of carbon fiber is also a disadvantage for civil applications. The composite oxidizes in air at temperatures above 450 °C.

3.2.6 Factors Affecting Mechanical Properties of the Composites

The properties of FRP-reinforced composites depend on the mechanical properties of matrix and fibers used in the composite, properties of the fiber–matrix bond, fiber orientation within the matrix material, and volume ratio of fiber to matrix and cross-sectional area of fiber.

3.2.6.1 Properties of Matrix and Fibers

Properties of matrix and fibers are already discussed in previous sections. Fibers with high strength and high stiffness are inserted and merged into the low modulus continuous polymeric matrix in fibrous polymeric nanocomposites; each of the individual phases must accomplish particular functional requirements based on their mechanical properties so that the system containing them may succeed satisfactorily as a composite.

3.2.6.2 Properties of the Fiber–Matrix Bond

The behavior of a composite material is depended on the combined behavior of the reinforcing fiber, the polymer matrix, and the fiber/matrix interface. To attain superior mechanical properties, the interfacial adhesion via the fiber/matrix interface should be strong. Fibers are embedded into the matrix molecules by chemical reaction or adsorption, which determine the extent of interfacial adhesion. Good fiber–matrix interaction results strong interface and overall a good composite.

3.2.6.3 Fiber Orientation Within the Matrix Material

In the case of FRP composites, the reinforcing fibers constitute the backbone of the material, and they determine its strength and stiffness in the direction of fibers. Fibrous reinforcement represents physical rather than a chemical means of changing the composite to suit various engineering applications. Discontinuous fibers or whiskers having either random or biased orientation are mainly used to improve properties or lower the cost of isotropic materials. Continuous fiber composites can be either single layer or multilayered. Orthotropic composites with long fibers in one direction are called continuous fiber reinforcement, and composite in which short or staple fibers are embedded in the matrix has discontinuous fiber reinforcement. Higher mechanical properties can be obtained in a particular composite by varying the fiber orientation than by fiber aspect ratio.

The composite is stronger along the direction of orientation of the fibers and weakest in a direction perpendicular to the fiber. Figure 3.9 depicted different fiber

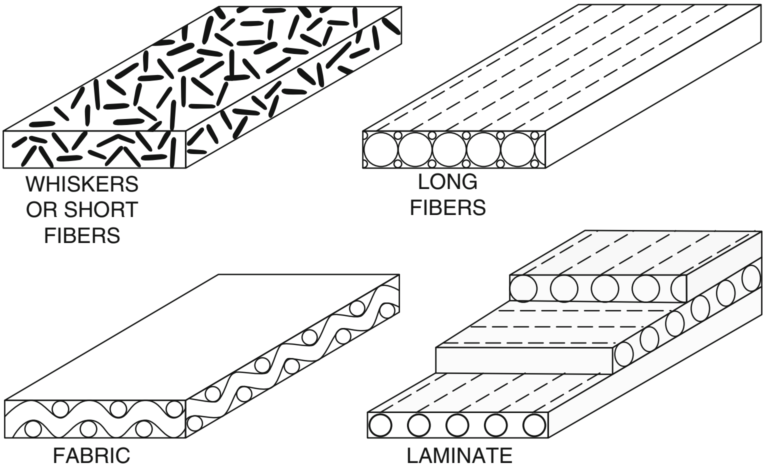
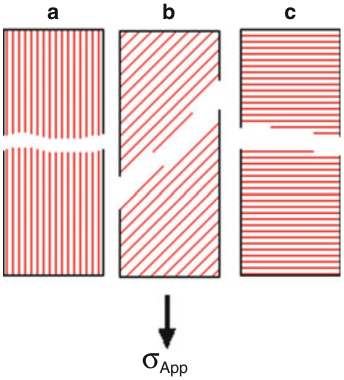


Fig. 3.9 Different fiber orientation

Fig. 3.10 Effect of fiber orientation on tensile strength



orientation, and Fig. 3.10 shows the effect of fiber orientation on tensile strength. In continuous fiber composites, fibers are oriented in one direction to produce enhanced mechanical strength. In short fiber composites, the length of short fiber does not allow to entangle with each other. Hence, moderate strength composite is obtained, and well-dispersed short fibers provide uniform reinforcement. To achieve effective strengthening and stiffening, the fibers must be larger than a critical length, which is defined as the minimum length at which the center of the fiber reaches the ultimate (tensile) strength when the matrix achieves the maximum shear strength.

A laminate is fabricated by stacking a number of laminae in the thickness direction. Multilayered composite, i.e., laminate, is fabricated by stacking polymer and fibers alternatively in the thickness direction, and it gives good compression strength. But for flexural strength, the laminates with fiber orientation of 45° have more flexural strength than the laminates with 0° or 90° orientation for the same type of the fiber reinforcement. Matrix and fiber behavior follows iso-strain approximation until the onset of failure; it is possible to predict the tensile and compressive strength in the fiber direction [89Sel]. The damage tolerance of polymeric materials can be enhanced by improving the interlaminar properties of the polymer composites [02Wan].

3.2.6.4 Volume Ratio of Fiber to Matrix

Short carbon fiber shows a great strengthening and toughening effect for a low volume percentage of fibers (3–5 vol.%). Although composites formed under pressure usually have a higher fiber volume fraction, and the strengthening and toughening effect of short carbon fibers reduces. The reason behind this may be due to damage in fibers, formation of high shear stresses of intersect between fibers and strong interface cohesion of fiber/matrix. The predominant strengthening and toughening effects at low volume % may be due to the formation of the reasonable network structure of short carbon fibers as well as the apparent fiber bridging and pulling out [09Lin].

3.2.6.5 Fiber Cross-Sectional Area

Composite with reduced fiber diameter provides considerably more fiber surface area than the composite with higher fiber diameter where in both cases keeping the fiber volume fraction same. The increased surface area can help to minimize the ineffective fiber length. The ineffective fiber length representing the fiber region where the axial stress is not fully developed and ineffective fiber length reduction will balance the imperfect bonding between the fiber–matrix interface. Therefore, uniform stress distribution will be found with less overall mechanical damage. Composites with reduced fibers also offered reduced shear stress developed in the fiber–matrix interface. Therefore, composite materials with reduced diameter fiber are expected to offer higher strength than a conventional composite prepared with the same volume fraction of fiber [10Hos].

3.2.7 Applications of Carbon Fiber-Reinforced Composite in Structure and Construction

In recent years, carbon fiber-reinforced composites have emerged as a potential solution to the problems associated with infrastructures. The usual applications of carbon fibers are strengthening constructions, retrofitting of old structures, reinforcing precast concrete. Carbon fibers are also utilized as a replacement for steel, pre-stressing materials and strengthening cast-iron beams. Its high strength, light weight and resistance to corrosion make it an ideal for structural engineering applications. The composites are used in form of tension elements, ropes, dismountable and permanent shuttering, and prestressing bars.

3.2.7.1 Strengthening of the Constructions

Since 1982, FRP composites have been successfully used to strengthen concrete structure, and these days applying carbon fibers in building engineering is one of the most common alternatives [95Mei]. Carbon fibers are applied in fabric or pultruded strip forms, and the product is a thin strip of unlimited length having unidirectional fibers. These prefabricated strips are glued to the surface, and the fabrics improve strength and rigidity. The glue is responsible only for the contact between the carbon strip and the surface of the member. The main advantages of this reinforcing for wooden structures in comparison with traditional methods are fast and easy to install, possible to make it invisible. Bidirectional canvas gluing onto the bottom surface of the beam is also very popular where tensile stresses cause cracks along the element axis. In another way, resin layer is applied on the surface, and the fibers are put into this resin layer in situ in the form of fabrics. The fabrics are covered again with a resin layer. This procedure can be repeated several times and provide strength to the construction [03Has]. Strengthening of the concrete deck in the transverse direction by this method is accepted in Europe, Japan, and North America due to its less electrolytic corrosion, high strength, low transportation cost, easy application even in small spaces, no need for scaffolding to support the strengthening materials during hardening of adhesive, no limitation in length, and reduction of height below the strengthened member.

3.2.7.2 Using of Carbon Fiber in Precast Concrete

This field is comparatively new and rapidly developing. Carbon fibers in precast concrete started to appear in quantity production from 2003. Now it is a very common material for precast elements in the USA. Carbon fiber used in precast concrete gives noncorrosiveness, low weight, and thermal efficiency and due to these carbon fiber grid is very useful in the panel faces to replace steel mesh reinforcement and as a mechanical link to the outer and inner sections of the concrete wall as shown in Fig. 3.11.

3.2.7.3 Carbon Fiber in Bridge Construction

A prospective field of applying carbon fiber is bridge construction. Easier, faster, and more economic installation makes this technique well conventional, and these types of bridges are applicable in any extreme environment (de-icing salts, chemicals). Minimal maintenance requirements, through-life costs, and disruption are the extra advantages of using carbon fiber in bridge [06Ban]. Carbon fiber-reinforced composites are thermally stable which may remove need for expansion joints. So, since 1992 there have been built several carbon fiber bridges. In Fig. 3.12 carbon fiber bridge in Spain is shown.

3.2.7.4 Seismic Retrofit

One of the most severe problems faced by the earthquake engineers in the past decades was large number of masonry buildings in seismic regions that were damaged due to earthquake. A large lateral cyclic earthquake force can degrade strength of concrete and reinforcing bar that can result in premature failure of

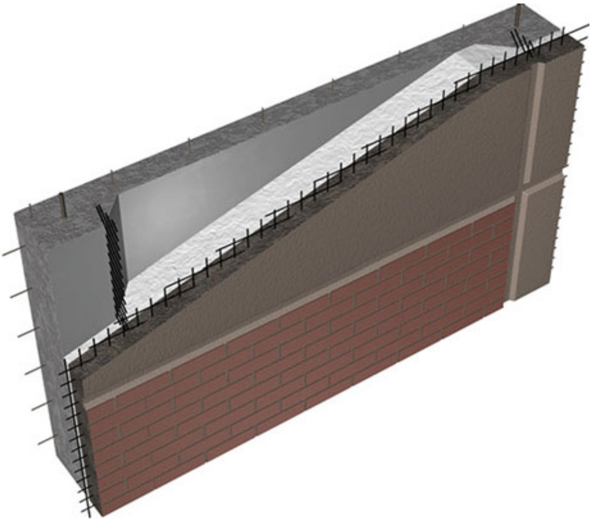


Fig. 3.11 Carbon fiber used in precast concrete [14Acs]

Fig. 3.12 Carbon fiber bridge in Spain [14Bus]

column. Seismic rehabilitation techniques for civil construction involving steel jacketing, concrete jacketing, and fiber-reinforced composite jackets for columns have been developed. Retrofit of columns to withstand earthquakes is a recent and extensive challenge for civil engineers. Seismic resistance of retrofitted columns by carbon fiber reinforcement improves significantly because of confining action of the carbon fiber jacket wraps [96Chr, 97Saa]. The technique has been examined to recover displacement ductility as well as strength [08San]. The repaired structures also exhibit lower rate of deterioration under large reversal cyclic loading than the virgin columns. Fiber-reinforced wraps consisting of carbon fibers, bonded with epoxy resins, have been successfully applied for seismic rehabilitation of bridge piers in the USA and Japan [92Muf].

3.2.7.5 Other Uses of Carbon Fiber

Carbon fibers can also be used for construction of fiber-reinforced plastic profiles. These high-strength aggregates with low weight and low deflection make this solution suitable for construction in intricate structures. High-loaded floors and roads can be constructed by carbon fiber because of low thermal conductivity in comparison with steel and good cohesion with concrete. In fiber–cement, carbon fibers replace asbestos, because carbon fiber can reduce inhalation problems. Considering all its very properties, it can be used to repair dams, tubes, high pressure pipes, and historic monuments.

3.3 Clay- and Carbon-Based Polymer Nanocomposites Used in Road Application

It is widely recognized that transport infrastructure plays a key role in economic growth and development of a country. In India, flexible pavements constitute over 95 % of total road network. Bitumen is widely used as a binder of mineral aggregates for flexible pavement construction. The rapid growth in traffic in terms of commercial vehicles, overloading of commercial vehicles, and significant variation in daily and seasonal temperatures are the causes of early development of rutting and cracking in the bituminous layers. Bituminous binders deform when subjected to loads. The tensile deformation is responsible for the fatigue damage and consequently results in the fatigue failure of the pavements. Similarly, compressive deformation causes permanent deformation or rutting [03Rea]. Bituminous pavements also get damaged by temperature and moisture. Moreover, it is also observed that the entry of water through the surface cracks during monsoon season leads to the rapid deterioration of the bituminous surfacing.

Nanoclay modifications of bitumen help to increase the stiffness and aging resistances. Nanoclay modification improves the rutting resistances of bitumen as well as cyclic fatigue resistance [11Zha]. The effective use of a montmorillonite (MMT) on properties of styrene–butadiene–styrene copolymer modified bitumen by melt blending increases the viscosity and gives higher complex modulus and lower phase angle, implying stiffer and more elastic asphalt. Therefore, the nanoclay-modified bitumen was determined to have good rutting resistance compared to the virgin bitumen [07Yu].

Various fiber modifiers have been used widely to enhance material strength, fatigue resistance, and ductility properties of bitumen [96Ree]. Fibers offer an excellent potential for bitumen modification by carrying tensile forces and also help in preventing the formation and propagation of cracks because of their excellent mechanical properties [96Ser]. The use of carbon fiber shows consistency of the binder, increases stability and voids, and decreases the flow value of the pavement. Further, carbon fiber has the potential to improve structural resistance to distress occurring in road pavement due to traffic loads. Further, addition of fiber improves fatigue life and permanent deformation of bituminous mixtures by improving mix stiffness [08Jah]. Similarly, the incorporation of carbon nanoparticles in bitumen matrix increases the failure temperature, complex modulus, and elastic modulus values and improves aging properties [11Xia].

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Polymer Nanocomposites for Biomedical and Biotechnology Applications

4

Jasaswini Tripathy

4.1 Introduction

Polymer matrix–based nanocomposites have emerged as a new class of hybrid materials since last two decades and have attracted significant interest of researchers. Polymer composites represent efficient strategies to upgrade the structural and functional properties of polymers. The nanoparticles-reinforced polymer composites often show significant improvements in properties that cannot be achieved by using the polymer alone. Polymer nanocomposites are formed by combination of polymers and inorganic/inorganic nanofillers. Nanofillers are nanostructures which have dimension less than 100 nm and possess high interfacial area per volume [12Ray]. Most commonly, nanofillers are carbon nanotubes, silicates, metals, metal oxide, and ceramics. These fillers consist of different properties such as mechanical, chemical, thermal, electrical, etc. In this regard, the fundamental understanding and knowledge of the nanostructures are required for fabrication of materials for desired applications. The interaction between nanofillers and polymer matrix is the basis of mechanical and functional properties of polymer nanocomposites and by tuning various parameters and controlling the interaction between nanostructures and polymers, unique properties combinations can be achieved [07Lif, 11Gah].

By exploiting the inherent properties of nanomaterials and selecting suitable polymer matrix, a variety of nanocomposites materials have been generated with

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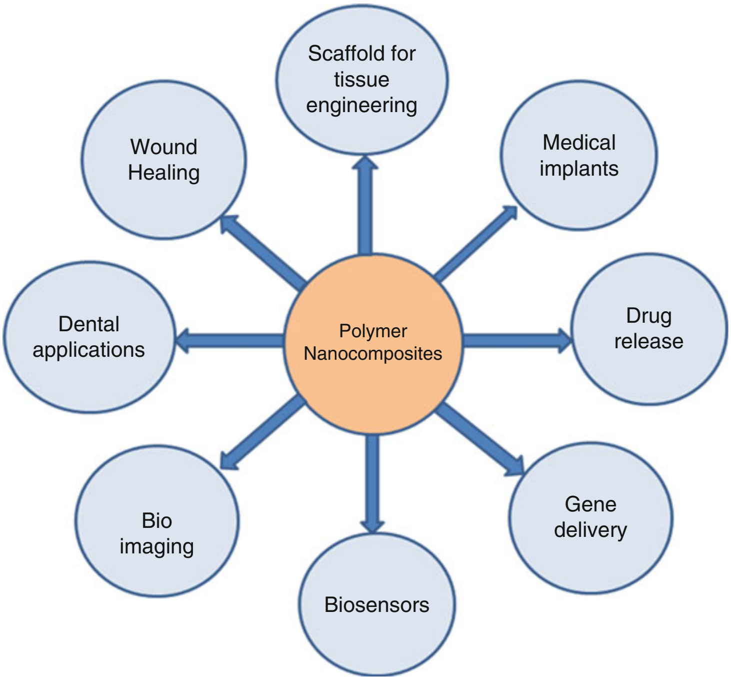
improvised properties. Current opportunities for polymer nanocomposites arise from the multitude of applications based on different functional requirements [08Pau]. The polymer-based nanocomposites have generated huge interest in many biomedical and biotechnological applications [14Goe]. Biomaterials based on polymer nanocomposites are field of interdisciplinary research which brings together collaborative efforts of materials science, nanotechnology, and biological science. A synergistic combination of physical, chemical, and biological properties of nanocomposites provides an exciting platform for designing and development of improved materials for biomedical applications [09Mit, 10Sat].

Polymer nanocomposites show improved mechanical properties, and thus can be used to replicate high performance materials such bone and silk [08Lee]. Nature offers strategies to mimic biological tissues containing hard and soft components. Biologically inspired materials can be fabricated by unique combination of soft polymer matrix and hard nanostructure; thus, these new composite materials are being developed by dispersing hard inclusions in polymer matrix [08Vai, 09Mit]. However, one of the key challenges faced during fabrication of polymer-based nanocomposites is uniform dispersion of nanofillers into polymer matrix for which different processing technologies have been used by researchers [05Dun]. Another key issue which needs to be addressed while fabricating nanocomposites for biomedical applications is biocompatibility factor. Thus by balancing mechanical properties, functionalities, and biocompatibility factors, polymer nanocomposites are finding many interesting applications in the emerging technologies such as tissue engineering, biomedical imaging, sutures, surgical implants, drug delivery-based applications, etc. [14Goe].

In tissue engineering, scaffold serves as a template and structural support for cell adhesion, proliferation, differentiation, and extracellular matrix formation [10Arm]. Replicating some physical properties of natural tissue and reproducing their complexity and efficiency are very challenging; thus, scaffold matrices have to be designed which not only resemble the structural and mechanical properties of a natural tissue but also imitate the signaling environment of the natural extracellular matrix (ECM). In this regard, polymer-based nanocomposites [14Ser] have been widely explored. These materials are applicable for hard and soft tissue engineering due to their unique mechanical and electrical properties. Apart from tissue engineering, polymer nanocomposites are also considered as potential candidates for drug delivery as they provide possibility to deliver large and controlled doses of therapeutic agents at the action site. The polymer-based polymer composites have been utilized in a myriad of bioapplications (Scheme 1). To achieve different functional requirements, these polymer-based nanocomposites are tailored with functionalities which open new possibilities in developing advanced biomaterials for various biomedical and biotechnological applications.

Here, in this chapter we focus on biomedical applicability of carbon nanotube (CNT), graphene, and nanoclay-based polymer nanocomposites. This chapter highlights applications of these polymer nanocomposites in emerging biomedical fields such as tissue engineering, drug delivery, etc.



Scheme 1 Biomedical and biotechnological applications of polymer nanocomposites

4.2 Nanofillers for Polymer-Based Nanocomposites

Polymer-based nanocomposites for bioapplications are fabricated by reinforcing nanofillers into biocompatible polymers which include both natural and synthetic polymers. This section presents three different nanofillers which are extensively used for the preparation of polymer-based nanocomposites:

1. Carbon nanotubes as fillers
2. Graphene as fillers
3. Nanoclay as fillers

4.2.1 Carbon Nanotubes as Fillers

Carbon nanotubes (CNTs) are allotropic forms of carbon discovered in late 1950s; however, the synthesis was first reported by Lijima [91Lij] and Bacon [60Bac]. The major methods adopted for synthesis of carbon nanotubes include laser ablation [96The], arc-discharge [97Jou], template-directed synthesis, chemical vapor deposition (CVD) [99Cas], and catalyst chemical vapor deposition (CCVD). However, CVD is the most commonly used method due to its low setup cost and high production yield. CNTs are either composed of monolayered graphene sheet (Single-walled carbon nanotubes, SWCNTs) or several concentric graphitic layers with multiwalled structure (multiwalled carbon nanotubes, MWCNTs). CNTs have fascinating electrical, mechanical, as well as thermal properties [14Ser]. They are known to have exceptional mechanical properties such as high Young's modulus and tensile strengths up to 63 GPa (10–100 times higher than steel) [96Tre, 00Yu], as well as thermal stability up to 2800 °C under vacuum [01Tho]. Due to their unique properties, these nanosized structures find wide application in many areas of material science including nanocomposites [12Wan].

CNTs have been recognized as effective reinforced materials for polymer nanocomposites because of their excellent mechanical, electrical, and surface properties such as high aspect ratio and enormous surface area. Incorporation of CNT significantly increases the mechanical strength of polymer matrix. In addition to the role of carbon nanotubes, the mechanical behavior of polymer nanocomposites are also dependent on polymer nature (amorphous/crystalline/semicrystalline). Also the adhesion between carbon nanotubes and the polymer matrix, and the homogenous dispersion of nanotubes in the polymer matrix are equally important in improving the properties [02Coo, 03Won] which is influenced by fabricating methods (melt blending/latex technology/in situ polymerization/solvent casting/). Integration of CNT as nanofiller in polymer matrix not only improves the physicochemical properties such as strength and flexibility [10Spi] but also adds new functionalities due to which they find diverse applications [14Ser]. Sometimes CNTs are functionalized to explore their potential in chemical and biological applications [12Mac]. They have been exploited for various biological applications such as the preparation of tips for atomic force microscopy, fuel-powered artificial muscles, and nanosurgical needles and biosensors, etc. [03Wan, 14Ser].

4.2.2 Graphene as Fillers

Graphene is a single layer two-dimensional material with a hexagonal-packed lattice having many unique properties such as high carrier mobility at room temperature [04Nov], high Young's modulus [08Lee], and excellent conductivity [08Bal]. Graphene can be synthesized by chemical vapor deposition (CVD) growth, mechanical exfoliation of graphite, or exfoliation of graphite oxide [10Dre]. Currently, graphene-based polymer nanocomposites are an exciting area of research due to the superior properties of graphene compared to polymers [09Xu]. Due to its high thermal and electrical conductivity, it is reported to be better nanofiller than other carbon-based polymer composites. The distribution of graphene layers in the polymer matrix and interfacial bonding between the graphene layers and polymer matrix are very important in determining the physicochemical properties of the nanocomposite. Since pristine graphene is not compatible with organic polymers and does not form homogeneous composites, graphene oxide (GO) sheets are more preferred [07Sta] as nanofiller for polymer nanocomposites. The remarkable property of graphene provides possibilities for various fields.

One such interesting area of research is biomedical applications of graphene-based polymer nanocomposites. Indeed, the number of publications on bioapplications of graphene-based nanocomposites has grown exponentially in recent years. Graphene-based polymer composites have been utilized in a myriad of bioapplications.

4.2.3 Nanoclay as Fillers

Nanoparticles derived for clay minerals have been considered as very effective reinforcing materials for designing polymeric nanocomposites. Due to their abundant nature, low cost, and interesting properties such as high strength, stiffness and high aspect ratio of individual platelets, clay-based polymer composites are used in different fields. Clay minerals include both natural clays (e.g., montmorillonite, hectorite, and saponite) and synthesized clays. Depending upon the nature of the components and processing conditions, layered clays filled into a polymer matrix form either conventional composite or nanocomposite. In case of conventional composite, polymer cannot intercalate into the galleries of clay minerals, whereas nanocomposites can further be divided into two types called as intercalated nanocomposites and exfoliated or delaminated nanocomposite.

In case of intercalated nanocomposites, monolayer of extended polymer chains is impregnated into the gallery of clay minerals resulting in an ordered multilayer structure with alternate polymer layers and clay platelets, whereas in exfoliated nanocomposites clay platelets are completely and uniformly dispersed in a continuous polymer matrix resulting in enhanced polymer–clay interaction [10Kil]. Clay-based nanocomposites exhibit strong interfacial interactions between the dispersed clay layers and the polymer matrix which leads to enhanced mechanical, thermal, and barrier properties over the virgin polymer.

The incompatibility between hydrophilic clay and hydrophobic polymer is one of the shortcomings, which often causes agglomeration of clay mineral in the polymer matrix. Therefore, surface modification of clay minerals is the most important step to achieve polymer nanocomposites. The unique layered structure and high intercalation capabilities of clay minerals allow them to be chemically modified to be compatible with polymers which are essential for development of clay-based polymer nanocomposites The selection of clay for polymer nanocomposites depends upon on their targeted applications.

One of the promising applications of these nanocomposites is in the field of biomedical and biotechnological arenas. Clay-based polymer nanocomposites have been investigated in many biomedical and biotechnological applications such as tissue engineering, drug delivery, biosensors, and biomedical devices. However, some of the major challenges to consider while developing materials for biomedical relevance include long-term biocompatibility and biodegrability issues.

4.3 Bioapplications of Polymer Nanocomposites

4.3.1 Biomedical Applications of CNT Polymer Nanocomposites

Recently carbon nanostructures-reinforced polymer nanocomposites have increasingly drawn attention of researchers for their use in biotechnology and biomedical field. They have been exploited for variety of biomedical applications. Particularly CNT-based polymer composites are widely investigated [14Ser]. A significant amount literature is available on nanocomposite made from polymers and nanotubes as biomaterials.

4.3.1.1 Tissue Engineering

The use of CNTs/polymeric composites as scaffolds for bone engineering has recently become a subject of interest. The scaffolds used for tissue engineering serves as substrates for cell adhesion, proliferation, differentiation, extracellular matrix (ECM) formation, and to guide tissue regeneration. The ideal scaffold for tissue regeneration should possess sufficient mechanical properties. In this regard, carbon nanotubes have the potential in providing the needed structural reinforcement for tissue scaffold [10Arm]. The much anticipated use of CNTs in these scaffolds is mainly to improve their overall mechanical properties and to promote and guide bone tissue regeneration. By integrating a small fraction of carbon nanotubes into polymer matrix, significant improvements in the mechanical strength of the composite is observed [05Che]. Wang et al. have shown that MWCNTs blended with chitosan significantly improved the mechanical properties compared with those of chitosan [05Wan]. The biological properties of CNT scaffolds have been confirmed by in vitro studies. Several cells types have been successfully grown on carbon nanotubes-based polymer composites. Jell et al. have reported synthesis of porous thermoplastic polyurethane–multiwalled carbon nanotubes (CNTs) foams by thermally induced phase separation (TIPS) method [08Jel]. They have shown that CNT incorporation significantly improved the compression strength and stiffness of the nanocomposite scaffold. Through in vitro studies, they found that osteoblast production of the potent angiogenic factor VEGF (vascular endothelial growth factor) increased in proportion to CNT loading which verifies the potential influence of the nanocomposite scaffolds. Shi et al. fabricated porous nanocomposite scaffolds using a thermal-cross-linking and particulate-leaching technique) [07Shi]. Through in vitro cultures, they confirmed that mesenchymal stem cells (MSCs) adhere and proliferate on all the PPF-SWNT scaffolds. Sitharaman et al. [08Sit] tested the biocompatibility of porous PPF-SWNT scaffolds in a rabbit model. They found that implants made of PPF-SWNTs displayed only mild inflammatory responses. The PPF-SWNT nanocomposite scaffolds showed significant bone ingrowth after 12 weeks of implantation with increased collagen matrix production (Figs. 4.1 and 4.2).

One of the careful considerations while fabricating carbon nanotube scaffold is uniform dispersion of carbon nanotube in polymer matrix to achieve desired electrical conductivity and mechanical strength. The uniform distribution of CNT in polymer matrix transfers the load from the matrix to the nanotube which is essential

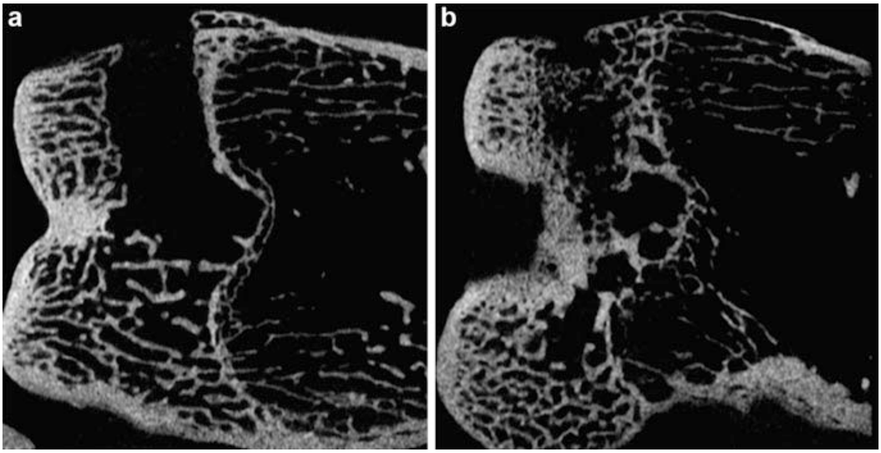


Fig. 4.1 Representative micro CT images of the rabbit femoral condyle 12 weeks after the implantation of either a (**a**) PPF or (**b**) US-tube/PPF scaffold (Adapted from Sitharaman (2008))

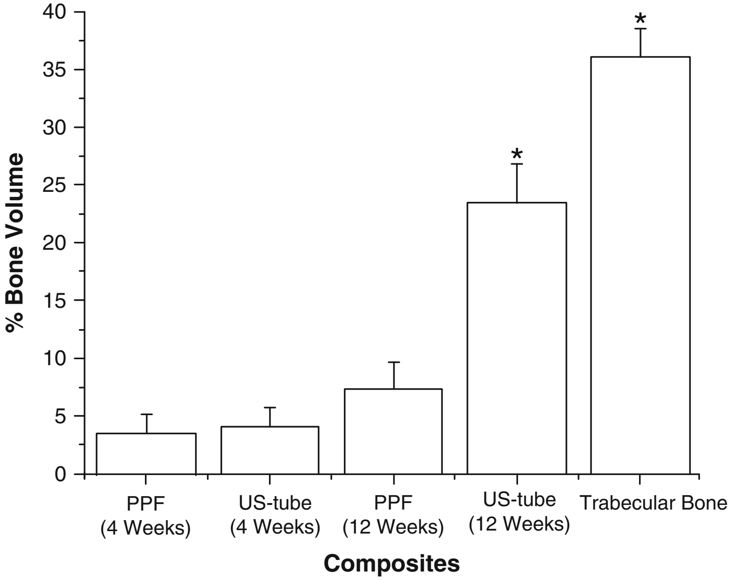


Fig. 4.2 Percent bone volume at the initial defect site after 4 and 12 weeks for each of the study groups, as measured from reconstructed three-dimensional micro CT images (Adapted from Sitharaman (2008))

for enhancing the mechanical and electrical properties of the composite. Different techniques have been explored to improve the CNT dispersion in different polymer matrix [10Arm]. Functionalization of CNT is also an effective route to increase the dispersing ability. Furthermore, the functionalization of CNTs increases water

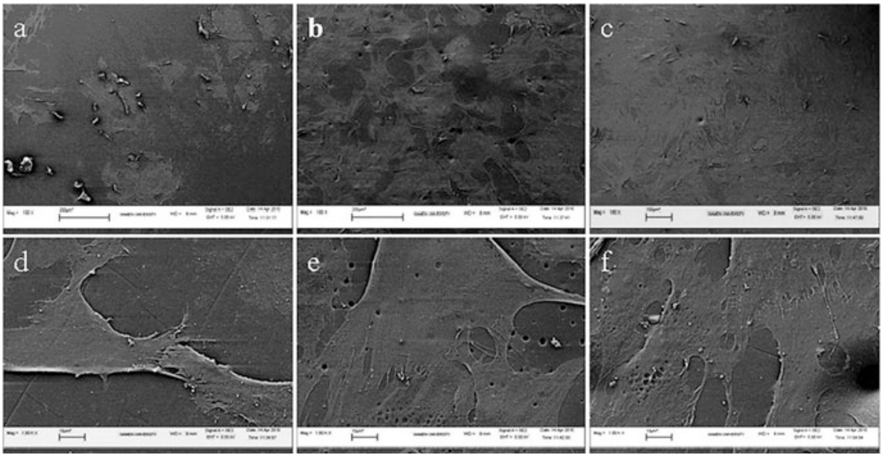


Fig. 4.3 SEM images of MSCs cultured on (**a**, **d**) smooth PLGA, (**d**, **e**) PLGA/MWCNTs, and (**c**, **f**) PLGA/c-MWCNTs films for 24 h at 100× magnification (**a**–**c**), and at 1000 × magnification (**d**–**f**) (Adapted from Lin (2011))

miscibility and biocompatibility of CNT. Covalent or noncovalent addition of various chemical functional groups can be done to the side walls and tips of CNTs to control the interaction between polymer and carbon nanotube. The nature of the functional group at the CNT surface plays a determinant role in the mechanism of interaction with cells. Lin et al. fabricated nanocomposites by incorporating carboxyl-functionalized multiwalled carbon nanotube (c-MWCNT) into poly(lactic-co-glycolic acid) (PLGA) matrix [11Lin]. Their observations revealed that c-MWCNTs gave a better dispersion than unmodified MWCNTs in the PLGA matrix with increased mechanical properties of the nanocomposites. They have shown that 7-week period in vitro degradation test accelerated the hydrolytic degradation of PLGA. In addition, the cells could adhere to and spread on films via cytoplasmic processes. Their results demonstrated that c-MWCNT-modified PLGA films were beneficial for promoting cell growth and inducing MSCs to differentiate into osteoblasts (Fig. 4.3).

Shi et al. fabricated nanocomposite scaffolds by incorporating single-walled carbon nanotubes (SWNTs) in poly(propylene fumarate) (PPF) matrix. They showed that the functionalization of single-walled carbon nanotubes (SWNTs) increases the interaction between nanotubes and polymer matrix which in turn enhances mechanical properties [06Shi].

The electrical conductivity of CNS-based nanocomposites is used to direct cell growth due to their ability to conduct electricity stimulus into the tissue healing process. Khang et al. used the electrical conductivity of CNTs to increase the cell density on the on CNTs–polycarbonate urethane nanocomposite surface via electrical stimulation [08Kha]. Supronowicz et al. have provided evidence that electrical stimulation delivered through nanocomposites of poly(lactic acid) and MWCNTs promotes osteoblast functions [02Sup].

For the preparation of 2D CNT films and fibers, the techniques involved are mainly layer-by-layer (LbL) deposition and solution–evaporation technique, [05Wan, 10Byr], whereas for the preparation of 3D CNT-based scaffolds the methods such as freeze-casting and electrospinning [14Ser] have been opted which generally produce scaffolds with controlled and interconnected porosity. Concerning nerve tissue repair, Kabiri et al. reported CNTs/PLLA fiber scaffolds as a as potential candidates for neural tissue regeneration [12Kab].

4.3.1.2 Other Bioapplications

Other biomedical and biotechnological applications of CNT-based polymer nanocomposite include drug delivery, wound healing development of chemiresistors [10Cho], dental composites [13Bor], and microcatheters [05End].

4.3.2 Graphene-Based Polymer Nanocomposites

Graphene has been exploited for diverse applications due to its unique properties. Of particular interest is a biological application of graphene which is well documented. Graphene oxide (GO) is more widely used as compared to graphene due to the presence of carboxylic, epoxy, and hydroxide groups, which provide opportunity for functionalization. GO has been functionalized with many biocompatible polymers for requisite biological applications. Graphene-based polymer composites have been investigated for various biomedical applications. They are anticipated to be promising materials to be used for tissue-engineered scaffolds, drug delivery vehicles, biosensors, etc.

4.3.2.1 Tissue Engineering

Due to enhanced mechanical and electrical properties, graphene-reinforced polymer composites hold immense potentials for tissue engineering scaffolds. The graphene-based polymer nanocomposites have been reported to be biocompatible and beneficial for the growth of the cells [11Par]. Sayyar et al. prepared graphene/polycaprolactone composites by covalently linking the polymer to the graphene chains which resulted in improved conductivity and mechanical properties. The growth of Fibroblast (L-929), neural (PC-12) and muscle (C2C12) cell lines on cPCl–CCG materials were assessed by comparing with growth of these cell types on pristine PCl [13Say]. They found that all cell lines proliferated on PCl, cPCl–CCG 0.5% and 5 % in a similar way to tissue culture plastic suggesting the potential applications of fabricated nanocomposite for tissue engineering (Fig. 4.4). In a similar approach GO–chitosan hydrogel scaffolds prepared by covalent linking chitosan with graphene exhibited better mechanical properties and lower degradation rate. In addition, there was significant improvement in cell adhesion, differentiation, proliferation, and calcium phosphate deposition of mouse preosteoblast MC3T3-E1 cells on the hydrogel [11Dep]. Zhang et al. reported that the tensile strength and compressive strength of PVA-based hydrogels were significantly enhanced by incorporating GO without affecting their cytocompatibility [11Zha].

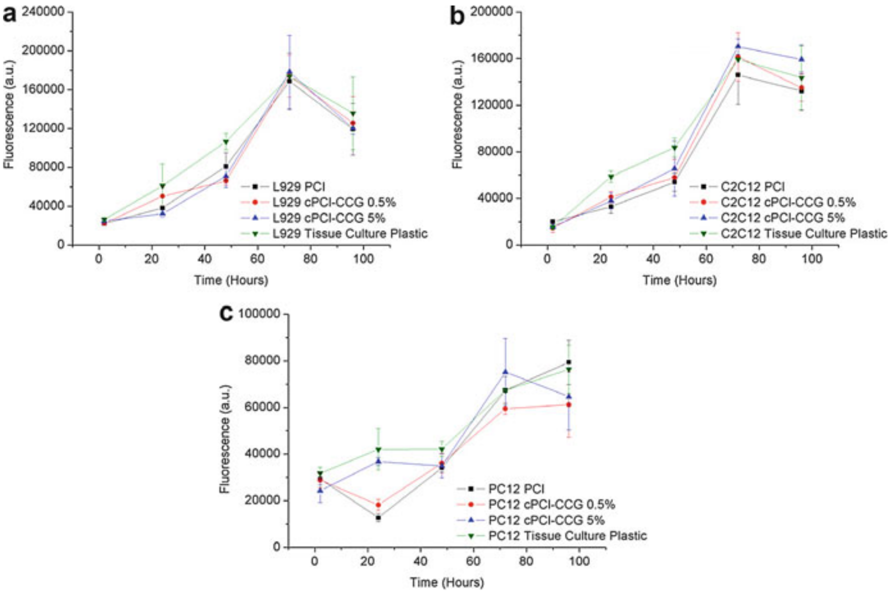


Fig. 4.4 Growth curves of three cell lines on PCl, tissue culture plastic, and cPCl–CCG materials. Fibroblasts (**a**, L-929 *cell line*), muscle cells (**b**, C2C12 *cell line*), and neural cells (**c**, PC12 *cell line*) all adhered to and proliferated on the materials for 72–96 h (Adapted from Sayyar (2013))

In another study, graphene-reinforced chitosan films did not show any toxicity when tested on murine fibrosarcoma L929 cell culture. The mechanical properties were also enhanced [10Fan]. Recently, Shin et al. fabricated 3D composite scaffolds from gelatin methacrylate and GO [13Shi]. The incorporation of GO into hydrogels enhanced their mechanical and electrical properties without affecting encapsulated fibroblast cells. Lu et al. [12Lu] fabricated chitosan–PVA nanofibrous scaffolds containing graphene. Further, they explored wound healing property of composite with and without graphene along with control (no scaffold) and found that the samples containing graphene healed completely and at a faster rate in both mice and rabbit. The wound healing property of graphene composite was attributed to free electron in graphene which inhibits the prokaryotic cell multiplication. This was further confirmed by performing antibacterial study on *E. coli*.

4.3.2.2 Drug Delivery

In addition to tissue engineering, the graphene-based polymer composites were found to be potential candidates for other biomedical applications including drug delivery. They are exploited for loading poorly soluble drugs due to their high surface area, π–π stacking, and hydrophobic interactions of graphene.

A number of studies have been reported on applications of chitosan and graphene nanocomposite for loading various drugs like 5-fluorouracil [11Ran] and camptothecin (CPT) [11Bao]. Liu et al. successfully loaded doxorubicine (DOX), an anticancer drug, into graphene nanosheets (GS) using gelatin as a reducing and functionalizing agent

[11Liu]. Gelatin–GS–DOX exhibited higher drug loading capacity due to large surface area and relatively higher π interactions. The Gelatin–GS–DOX complex also showed high toxicity towards MCF-7 cells through endocytosis. Sun et al. [08Sun] fabricated targeted delivery system by conjugating rituxan (CD20+ antibody) with polyethylene glycol–nanographene oxide (PEG–NGO). Loading of doxorubicin (DOX) onto PEG–NGO conjugate was favored due to the noncovalent π–π stacking and in vitro pH-dependent drug release was studied.

Kim et al. developed stimuli-responsive nanocarrier for intracellular cytosolic delivery of DOX by functionalizing rGO with PEG and branched polyethylenimine (BPEI) [13Kim]. DOX was released in response to near infrared (NIR), acidic pH, and high intracellular levels of glutathione (GSH). In another study [12Dem], DOX-loaded PEG–GO nanocomposites were developed and released in response to GSH.

Miao et al. [13Mia] demonstrated successful codelivery of anticancer drug doxorubicin (DOX) and photosensitizer (Ce6) using polyethylene glycol-grafted graphene oxide (pGO). They revealed that pGO nanosheets increased the cellular uptake as well as tumor tissue accumulation of Ce6, compared to treatment with free drugs (Fig. 4.5).

4.3.2.3 Gene Delivery and Bioimaging

Graphene-based polymer nanocomposites have also been explored for other biomedical and biotechnological applications such as gene delivery. For the purpose of gene delivery, Chen et al. functionalized graphene with cationic polymer polyethylenimine (PEI) [11Che]. PEI acts as a nonviral gene vector due to its strong electrostatic interactions with negatively charged phosphates of RNA and DNA. However, it shows low biocompatibility and high toxicity which limits its use. It was revealed that PEI–GO exhibited gene delivery high transfection efficiency and lower cytotoxicity compared to PEI alone. Kim et al. complexed PEG–BPEI–rGO with plasmid DNA for photothermally controlled gene delivery. The complex did not show any cytotoxicity to PC3 and NIH/3 T3 cells. The presence of rGO accelerated endosomal membrane disruption led to higher transfection efficacy when subjected to NIR irradiation [13Kim].

Graphene-based nanocomposites have also been fabricated for bioimaging purposes. Shen et al. [12She] prepared a multifunctional nanocomposite as MRI probe by combining PEG–functionalized GO complex and gadolinium–diethylenetriamine-pentaacetic acid–poly(diallyldimethylammonium)chloride (Gd–DTPA–PDDA). GO–IONP (superparamagnetic iron oxide nanoparticles) functionalized with PEG have been successfully used for drug delivery and bioimaging applications. [12Ma].

4.3.3 Clay-Based Nanocomposites

Silicate-based polymer nanocomposites have been anticipated as the next-generation materials for various biomedical applications due to the enhanced surface interactions of silicate nanoparticles and polymer chains [12Gah].

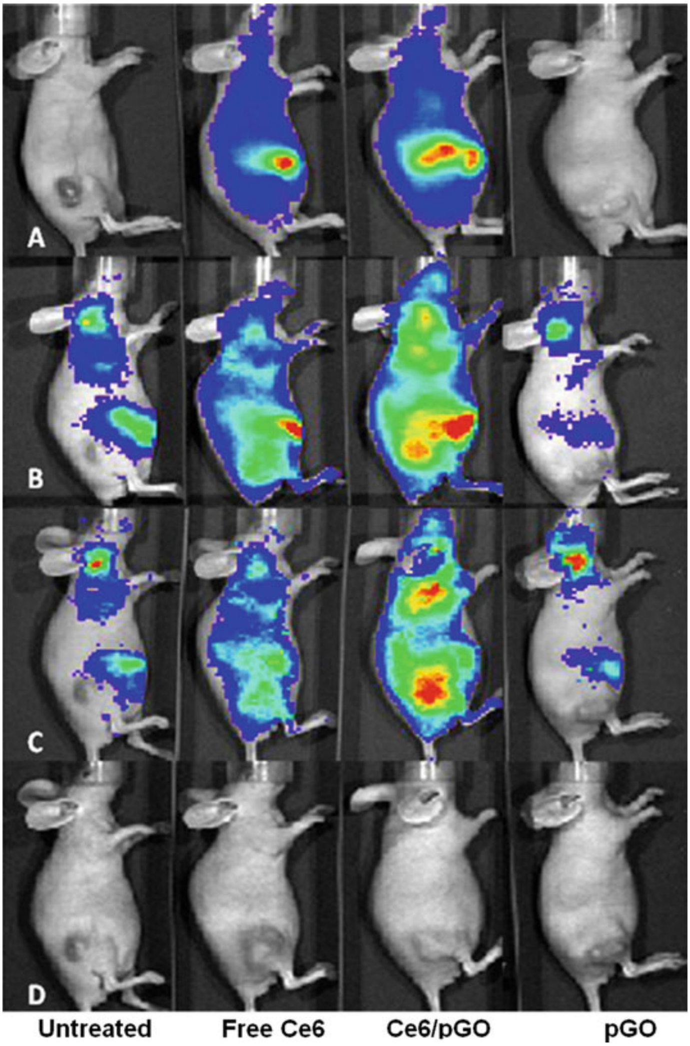


Fig. 4.5 In vivo biodistribution of pGO nanophysisorplexes. SCC7-bearing mice were systemically treated with pGO, free Ce6, Ce6/pGO, or with Ce6/Dox/pGO (Ce6 10 mg/kg and Dox 5 mg/kg). After 1 h (**a**), 24 h (**b**), and 48 h (**c**), the in vivo distributions of Ce6 fluorescence were visualized using a molecular imaging system. (**d**) Optical images are provided for location of tumors (Adapted from Miao 2013)

4.3.3.1 Tissue Engineering

Nanoclays (synthetic silicates) are widely used to reinforce polymer to improve physical and mechanical properties of polymeric matrix [10Wu] due to their anisotropic and high aspect ratio morphology. The physical and chemical properties of nanocomposite matrix can be controlled by addition of nanoclay to polymeric matrix. Nitya et al. have shown that the incorporation of halloysite nanoclay within

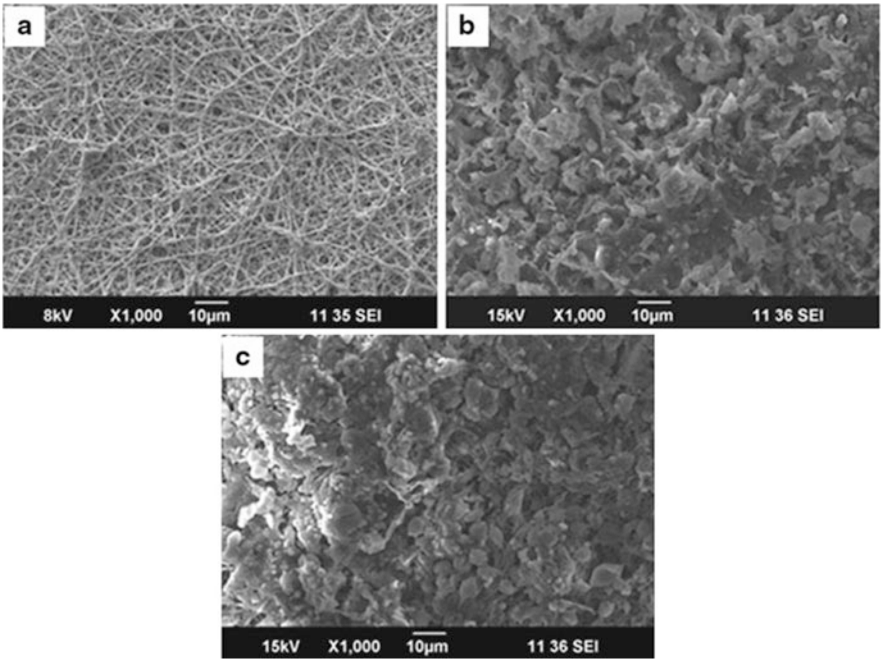


Fig. 4.6 SEM images of mineralized PCL nanocomposite scaffolds: SEM images showing mineralization after 21 days in SBF on a PCL, b PCL/4 % NC, and c PCL/6 % NC composite scaffolds (Adapted from Nitya (2012))

the PCL scaffolds not only increased the mechanical strength but also the protein adsorption and cell adhesion of the nanocomposite [12Nit]. Their results indicated that the human mesenchymal stem cells (hMSCs) seeded on these scaffolds proliferated faster than in PCL scaffolds (Fig. 4.6).

Gaharwar et al. have they have shown that silicate nanoparticles (Laponite RD) can be used to effectively control the adhesion, spreading, and proliferation of fibroblast and preosteoblast cells on silicate cross-linked PEO surfaces [10Gah]. In a similar study, they have revealed through in vitro cell culture studies that increase in silicate concentration in silicate cross-linked poly(ethylene oxide) (PEO) nanocomposites enhanced the attachment and proliferation of human mesenchymal stem cells significantly [12Gah].

In a recent study, nanoclay has been shown to induce osteogenic differentiation in hMSCs without using any growth factors [13Gah]. Ambre et al. have shown that MMT clay modified with 5-aminovaleric acid increases interlayer spacing and improves biocompatibility with human osteoblasts. They used MMT clay modified with 5-aminovaleric acid for preparing chitosan/polygalacturonic acid (ChiPgA) composite scaffolds [10Amb] In a similar approach, in another study they have reported fabrication of biopolymer (ChiPgA) scaffolds and films by intercalated nanoclays containing organomodified MMT clay with HAP (in situ HAPclay) for

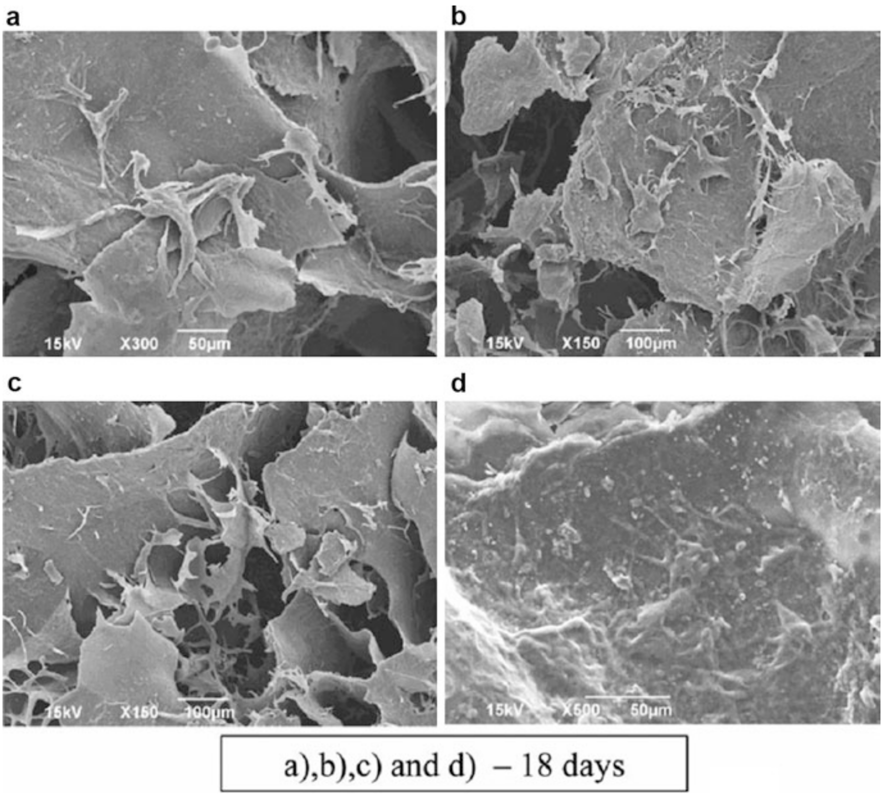


Fig. 4.7 (**a**–**d**) SEM micrographs of human MSCs on ChiPgA/in situ HAP clay scaffolds after 18 days of culture (Adapted from Ambre (2013))

bone tissue engineering. These HAPclay scaffolds were able to promote osteogenic differentiation of hMSCs [13Amb] (Fig. 4.7).

4.3.3.2 Drug Delivery

One of the biggest challenges in developing polymer-based drug delivery system is to control release of encapsulated or entrapped drugs. The therapeutic effects of the drugs and their biological activity can be optimized by controlling release kinetics of drugs. Silicate-based polymer nanocomposites show good barrier properties for diffusion of small molecules and thus can be applied for sustained drug release applications. Various drug delivery systems have been designed based on clay-based polymer nanocomposites for drug delivery-based applications.

Saha et al. [14Sah] fabricated film as well as nanofibrous web form of polyurethane/MMT clay nanocomposite as a delivery system for chlorhexidine acetate (CA), a bactericidal agent. Sustained release of drug was attributed to the presence of bulky and immobilized drug cation in the clay interlayer spacing which hinders the exchange of the cationic species present in the buffer media (Fig. 4.8).

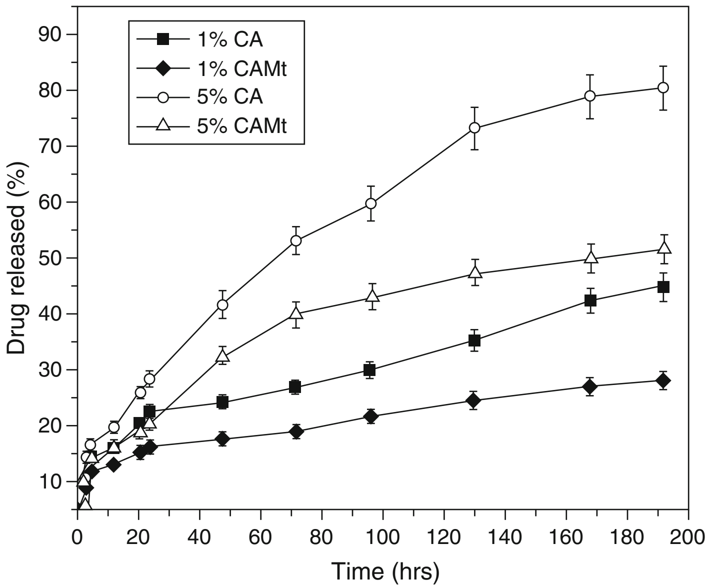


Fig. 4.8 Release profile of CA and CAMt-loaded film samples in PBS media at 37 °C (Adapted from Saha (2014))

Montmorillonite clay-based polyurethane nanocomposites have been explored as implantable drug delivery system. The therapeutics loaded nanocomposites were implanted in specific organs to control the release of a therapeutic agent to a specific target and to prevent different types of pathological processes [11Sil].

Lee and coworker [03Lee, 04Lee] fabricated clay-based poly (*N*-isopropylacrylamide) nanocomposite hydrogels and studied their drug release as well as swelling behaviors. It was concluded that clay in nanocomposites led to the decrease in swelling ratio and increase in strength of the nanocomposite hydrogels. In addition, they found that the release behavior of model drugs was largely depended on various factors including the content of clay and its intercalated agents.

Mishra et al. [14Mis] prepared nanocomposites of polyurethane by dispersing organically modified 2-D nanoclay followed by prepolymerization and subsequent chain extension using various chain extenders. These nanocomposites showed sustained release of drug as compared to the pristine PU. They have shown that by increasing the length of chain extender larger crystallites were formed which restricted drug diffusion due to barrier effect (Fig. 4.9).

A sustained release of dexamethasone drug was observed when organic modified silicate nanoparticles (Cloisite clay) were added to poly (ethylene-co-vinyl acetate) [56]. The drug release kinetics was suggested to be dependent on degree of dispersion as well as the aspect ratio of the silicate nanoparticles [03Cyp]. Li et al. have proposed Laponite nanoparticle-enriched alginate gels for the controlled delivery of cationic drugs [11Li] [14Mis].

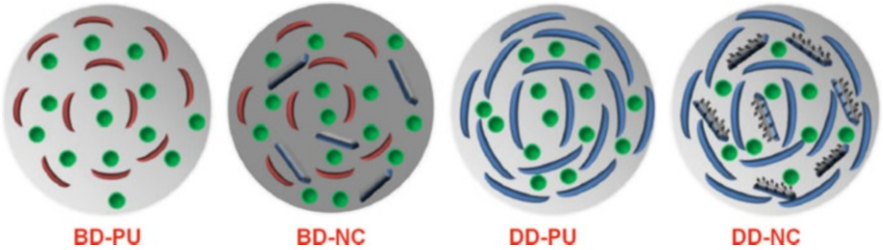


Fig. 4.9 Microstructure-controlled drug delivery. Crystallite size increases with the increase in aliphatic chain length of the chain extender. The formed with the chain extenders EG, BD, HD, and DD were designated as EG-PU, BD-PU, HD-PU, and DD-PU, respectively. BD-PU, which has a small crystallite size, shows prompt release, whereas DD-PU, which has larger crystallites, shows lower drug release. Moreover, in the case of DD-NC, the delayed diffusion of drug is controlled by crystallite size and 2D nanoclays as compared to that of BD-NC (Adapted from Mishra (2014))

4.3.3.3 Other Biomedical Applications

Clay-based polymer nanocomposites find diverse applications in biomedical field. For example, poly vinyl alcohol-clay-based polymer hydrogels have been exploited for wound dressing [07kok]. Bionanocomposites based on montmorillonite combined with HAP and chitosan have been evaluated as implants [08Kat]. Clay-based polymer composites have been also explored for food packaging applications [07Sor].

4.4 Concluding Remarks

There has been tremendous progress in synthesis of polymer-based nanocomposites due to the unique properties of nanostructured reinforcing materials. The synthesis and functionalization of nanofillers open new avenues for exploring their use in fabrication of polymer-based nanocomposites for bioapplications. These polymer nanocomposites have demonstrated improved properties significantly compared to the virgin polymer; thus, remarkable progress has been achieved in exploiting their use for emerging technologies such as drug/gene delivery and tissue engineering.

This chapter provides insights to multitude of bioapplications of polymer nanocomposites, thus expanding the range of applications from scaffolds for cell growth to biosensors. In spite of numerous efforts that have been taken to prepare polymer-based nanocomposites for bioapplications, there are still many challenges that need to be addressed to reach their full potential. While using these nanocomposites as biomaterial, the requisite criteria include biocompoatibilty and biodegradabilty and a host of other parameters which must be assessed properly with relevant preclinical studies to avoid false expectations. A careful selection of materials for developing nanocomposites and investigating their cellular level interactions will be instrumental for their biological applications.

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Polymer Nanocomposites for Environmental Applications

5

Tapas Ranjan Sahoo

5.1 Introduction

Nanotechnology is nowadays recognized to be one of the most promising areas for technological development. It broadly refers to manipulating matter at the atomic or molecular scale and using materials and structures with nanosized dimension, usually ranging from 1 to 100 nm. Due to their nanoscale size, nanoparticles show unique physical and chemical properties such as large surface area to volume ratios or high interfacial reactivity. Till now, increasing nanoparticles have been demonstrated to exhibit specific interaction with contaminants in waters, gases, and even soils, and such properties give hope for exciting novel and improved environmental technology [03Mas, 10Zha]. However, the small particle size also brings issues involving mass transport and excessive pressure drops when applied in fixed bed or any other flow-through systems, as well as certain difficulties in separation and reuse, and even possible risk to ecosystems and human health caused by the potential release of nanoparticles into the environment. An effective approach to overcoming the above technical bottlenecks is to fabricate hybrid nanocomposite by impregnating or coating the fine particles onto solid particles of larger size. In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different environmental applications.

Nature has mastered the use of nanocomposites, and researchers, as usual, are learning from their natural surroundings. In 1998, *Chemistry in Britain* published an

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article titled “Nano sandwiches” [98Ori], stating, “Nature is a master chemist with incredible talent”. Using natural reagents and polymers such as carbohydrates, lipids, and proteins, nature makes strong composites such as bones, shells, and wood. These are examples of nanocomposites, made by mixing two or more phases such as particles, layers, or fibers, where at least one of the phases is in the nanometer size range. Polymer nanocomposites (PNCs) are polymers (thermoplastics, thermosets, or elastomers) that have been reinforced with small quantities (less than 5 % by weight) of nanosized particles having high aspect ratios ($L/h > 300$). The widely used host materials for nanocomposite fabrication include carbonaceous materials like granular activated carbon [05Vau, 06Yin, 08Jan, 08Zhu, 09Jan, 11Jia, 12Nie], cellulose [05Guo, 08Con, 08Hun, 11Tak], diatomite [01Degs, 09Zen, 11Cal], silica [04Hir, 07Bad], sands [94Sze, 01Han], and polymers [00Suz, 02Cha, 02Lee, 02Wan, 03Sin, 04Che, 04Zha, 11Che]. The host materials of larger particle size greatly improve the permeability and separation of the resulting nanocomposites for facile operation. Also, they help us to inhibit the aggregation of the inorganic nanoparticles encapsulated therein due to the steric effect caused by their rigid matrixes. In recent years, more and more nanocomposites have been developed for efficient remediation of contaminated environment. But, the polymeric hosts are particularly an attractive option partly because of their controllable pore space and surface chemistry as well as their excellent mechanical strength for long-term use. The resultant polymer-based nanocomposite (PNC) retains the inherent properties of nanoparticles, while the polymer support materials provide higher stability, processability, and some interesting improvements caused by the nanoparticle–matrix interaction. The generally used nanoparticles include zero-valent metals [00Pon, 05Lin, 06Guo, 07Xio, 09Lio, 10Liu], metallic oxides [02Kat, 02Man, 02Zou, 03Dem, 05Cum, 07Bla, 07Che, 07Syl, 07Vat, 08Mol], biopolymers [96Sil, 05Sha, 06Jor, 07Tri, 09Chi], and single-enzyme nanoparticles (SENs) [03Kim, 06Kim, 06Yan, 07Dar, 08Yan]. These nanoparticles could be loaded onto porous resins [01Pon, 02Kat, 02Zou, 05Cum, 07Bla, 07Che, 07Hua, 07Syl, 09Lin], cellulose or carboxymethyl cellulose [05Guo, 05Kem, 08Wil], chitosan [07Yan, 09Zhu], alginate [02Zou, 07Kim, 09Chi, 09Ngo] etc. The choice of the polymeric supports is usually guided by their mechanical and thermal behavior. Other properties such as hydrophobic/hydrophilic balance, chemical stability, biocompatibility, optical and/or electronic properties, and chemical functionalities (i.e., solvation, wettability, templating effect, etc.) have to be considered to select the organic hosts [03Sin]. Highly cross-linked porous polystyrene adsorbents have proved to be ideal support materials, and hybrid sorbents based on surface charged polymeric supports (e.g., cation or anion exchangers) were found to exhibit more favorable sorption towards trace target metals. This is because the immobilized charged groups on a polymeric matrix would greatly enhance metal permeation and preconcentration prior to effective sorption by inorganic particles; the phenomenon is the so-called “Donnan membrane effect” [10Pan, 10Sar, 11Zha]. Polymer/layered nanocomposites in general can be classified into three different types, namely: (i) *intercalated* nanocomposites, (ii) *flocculated nanocomposites*, and (iii) *exfoliated nanocomposites*. In the first case, polymer chains are inserted into layered structures such as clays, which occur in a crystallographically regular fashion, with a few nanometer repeat distance, irrespective of the ratio of polymer to layered structure. In the second case, flocculation of intercalated and stacked layers to some extent takes place due to the hydroxylated edge–edge interactions of the clay layers. Finally, separation of the individual layers in the polymer matrix occurs in the third type by average distances that depend only on the loading of layered material such as clay. In this new family of composite materials, high storage modulus, increased tensile and flexural properties, heat distortion temperature, decrease in gas permeability, and unique properties such as self-extinguishing behavior and tunable biodegradability are observed, compared to matrix material or conventional micro- and macrocomposite materials. This chapter gives a brief description on the recent progress in synthesis and characterization of these environmentally benign PNCs as well as their performance in environmental remediation, pollutant sensing and detection, cleaner production, and so on. Besides, the forthcoming development in the field was also discussed.

5.2 Preparation of Polymer Nanocomposites

Various techniques have been developed and applied for preparation of PNCs. According to the formation processes of the nanocomposites, they could be generally divided into two categories. Those are ex situ (direct compounding) and in situ synthesis. Ex situ method of synthesis can be obtained by first synthesizing the nanoparticles and then dispersing them in a polymer solution or three-dimensional matrix. This method of synthesis is a popular one because it does not set a limitation on the nature of nanoparticles and host polymer to be used. However, blending polymers and nanoparticles to afford homogeneous and well dispersed inorganic material in the polymer, pose significant challenges. To address these difficulties, a different method, the in situ process of synthesis, is utilized. In this process, the preformed polymer phase acts as a microreactor and metal and metal oxide nanoparticles are generated inside the polymer phase from a precursor that are transformed into the desired nanoparticles by a series of appropriate reactions. The process is gaining popularity for their technological advantages over the ex situ methods because particle size and morphology can be controlled with relative ease. A wide variety of hybrid nanocomposites can be prepared using the in situ process.

5.2.1 Ex Situ Synthesis

The ex situ process has been extensively used to fabricate PNCs because of its convenience in operation, comparatively low cost, and suitability for massive production. This method consists of physical entrapment of the nanoparticles in the polymer or biopolymer network. Nanofillers and polymer supporters are prepared separately at first, and then they are compounded by solution, emulsion, fusion, or mechanical forces [02Cha, 02Lee, 04Che, 04Zha]. Such encapsulation of nanoparticles also helps in the stabilization of nanoparticles by preventing them to agglomerate and form larger particles. This is a problem always encountered in the traditional method of nanoparticle formation, where nanoparticles are synthesized in a bulk solution. In addition, polymer degradation upon melt compounding and phase separation of nanophase from the polymer phase is sometimes severe. These limitations should be considered when using the direct compounding method to prepare PNCs. In general, the procedure of ex situ synthesis consists of mixing of the metal salt or preformed nanoparticles with the polymer solution followed by the casting of the suspension in the form of a membrane or cross-linking the suspension to create a three-dimensional framework. The film or the framework is later subjected to an oxidation/reduction step wherein the nanoparticles are formed from the precursor salt or complexes, followed by solvent evaporation.

Solvent mediated synthesis process has been used in the preparation of several types of PNCs for various uses. In this process, the nanoparticles are preformed and mixed with a solvent and a polymer solution. After the solvent is cast either in a form of membrane or coating on another surface, low grade heat is utilized to evaporate the solvent, leaving behind a hybrid nanocomposite material [04Bak, 04San, 07Ban, 07Cha]. Polymerization or copolymerization procedure was also used for the entrapment of metal or metal oxide nanoparticles [01Shu, 02Man, 08Far, 08Shi]. In addition to the synthetic polymers, biopolymers such as chitosan, alginate, etc., have been widely used for ex situ synthesis of the PNCs. Many of the biopolymers are soluble in acidified aqueous solution. The preparation of PNC containing biopolymer generally involves conditioning of the biopolymer in different physical shapes and entrapment of the nanoparticles within the various shapes [09Gui]. The process consists of two steps, namely: (i) polymer dissolution, and (ii) polymer neutralization, coagulation, or ionotropic gelation [07Maw, 08Kra, 09Esc]. This technique has been widely used for the preparation of spherical hydrogels. However, manufacturing of films, membranes, fibers, and hollow fibers can be done using specific extrusion equipment. Figure 5.1 shows some different physical forms obtained with chitosan. Various surface treatments to nanoparticles have been adopted in the synthesis procedure, and the compounding conditions such as temperature and time, shear force, and configuration of the reactor can also be adjusted to achieve good dispersion of nanoparticles in polymer matrices [02Wan]. Sometimes, appropriate dispersing agent or compatibilizers are added to improve the particle dispersion and/or miscibility and adhesion between the nanoparticles and the matrix [04Che, 08Yup]. Yu et al. [08Yup] reported an approach for synthesis of cellulose/TiO_2 nanocomposites in the presence of supercritical carbon dioxide. It was found that supercritical carbon dioxide influenced the interactions between the molecular chains of cellulose, and the titania particles were facilitated to access and impregnate into the crystalline structure of cellulose fibers through formation of hydrogen bonds with abundant hydroxyl groups of cellulose, resulting in a great improvement in thermal stability. Figure 5.2 depicts a simplified process for impregnation of supercritical CO_2 and TiO_2 nanoparticles into cellulose.

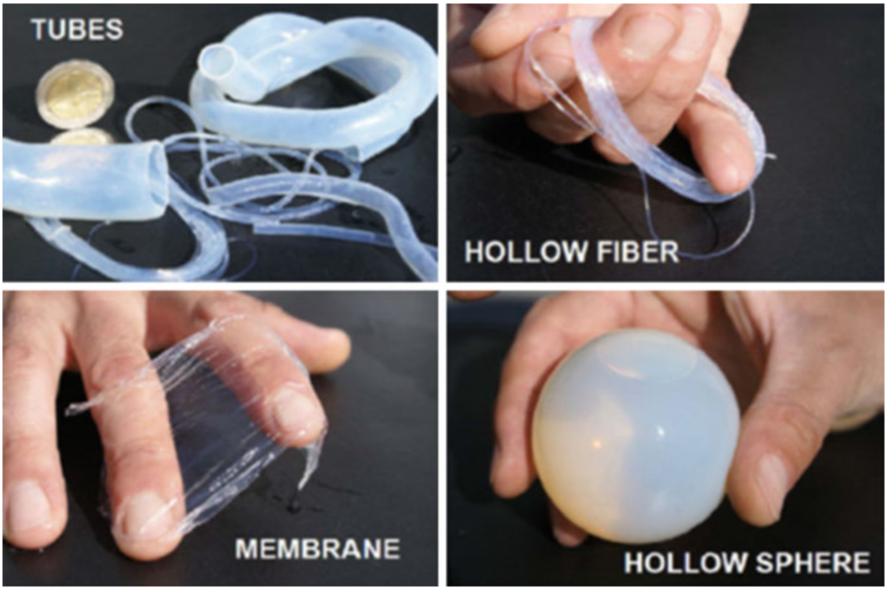

Fig. 5.1 Different physical forms in which chitosan can be fabricated

5.2.2 In Situ Synthesis

In contrast with the ex situ method of synthesis, in this method the nanoparticles of metal and metal oxides are synthesized within a preformed polymer framework or matrix. Considering the in situ approach, the combination of the wide number of functionalized polymers available and different types of nanoparticles that can be prepared gives rise to huge number of different PSNPs possible to be synthesized. The parameters that control the nature of the PSNPs are: (i) nature of the functional polymer, (ii) the type of nanoparticle precursor, (iii) the reaction that forms the nanoparticles, and (iv) the composition of the metal and metal oxide nanoparticles. In this process, the polymers serve as nanoreactors and provide confined medium for synthesis; also, they stabilize and isolate the synthesized nanoparticles preventing their aggregation. Although boundaries between the different processes of synthesis are very tight, according to different starting materials and fabrication processes, in situ synthesis can be generally classified as three types, as illustrated in Fig. 5.3.

1. Metal ions are preloaded within polymer matrix to serve as nanoparticle precursors first, where the ions are supposed to distribute uniformly. Then, the precursors are exposed to the corresponding liquid or gas containing S^{2-}, OH^{-}, or $Se^{2-}$to in situ synthesize the target nanoparticles [00Ton, 05San, 06Wua, 07Yan]. Tong et al. [00Ton] developed a sol–gel approach to prepare polyimide-TiO_2 hybrid films from soluble polyimides and a modified titanium precursor. The rate of the hydrolysis reaction of titanium alkoxide can be

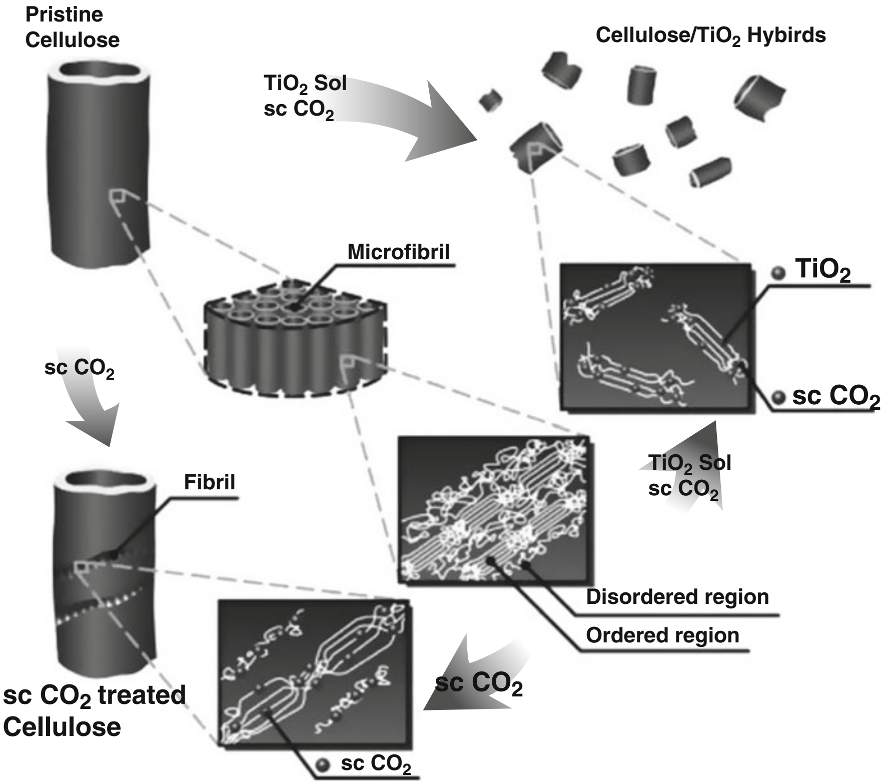

Fig. 5.2 Schematic model for impregnation of supercritical CO_2 and TiO_2 nanoparticles into cellulose [07Cha]

controlled by using acetic acid as a modifier. FTIR (Fourier transform infrared spectroscopy) and XPS (x-ray photoelectron spectroscopy) indicated that TiO_2 particles were well encapsulated in polyimide matrixes with particle size smaller than 60 nm.

2. Another similar approach employs the monomers of the polymeric hosts and the target nanofillers as the starting materials [06Gua, 06Tan, 11Wan]. Usually, the nanoparticles are first dispersed into the monomers or precursors of the polymeric hosts, and the mixture is then polymerized under desirable conditions including addition of appropriate catalyst. Increasing attention is paid to this method because it allows one to synthesize nanocomposites with tailored physical properties. Direct and well dispersion of the nanoparticles into the liquid monomers or precursors will avoid their agglomeration in the polymer matrix and thereafter improve the interfacial interactions between both phases. Tang et al. [06Tan], as an example, synthesized nano-ZnO/poly(methyl methacrylate) (PMMA) composite by in-site emulsion polymerization. To avoid the aggregation in the polymerization and to ensure their effective encapsulation, nano-ZnO particles

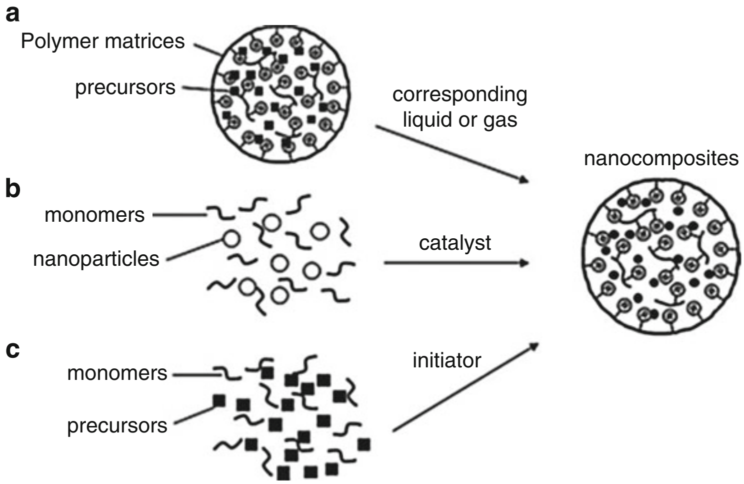

Fig. 5.3 Illustration of in situ synthesis process of PNCs. (**a**) Metal ions are preloaded within polymer matrix to serve as nanoparticle precursors first; (**b**) monomers of polymeric hosts and the target nanofillers as the starting materials; (**c**) nanoparticles and polymers are prepared simultaneously by blending the precursors of nanoparticles and the monomers of polymers with an initiator in proper solvent

were treated with the methacryloxy propyltrimethoxy silane (MPTMS) before they were added to the polymerization system.

3. Nanoparticles and polymers could also be prepared simultaneously by blending the precursors of nanoparticles and the monomers of polymers with an initiator in proper solvent [06Wan, 07Lia, 07Utr]. For example, Wan et al. [06Wan] prepared UV-curable, transparent acrylic resin/titania nanocomposite films by controlled hydrolysis of titanium tetrabutoxide in Span-85/Tween 80 reverse micelles and in situ photopolymerization of the acrylic monomers. AFM (atomic force microscope) images showed the inorganic domains (mean size 25.3–28.8 nm) were uniformly dispersed in the polymeric networks.

In many cases, biopolymer beads were impregnated with solutions containing precursor chemical and dried to produce PNCs. Molvinger et al. [04Mol] and DiRenzo et al. [05Ren] mixed chitosan beads with tetraethoxysilane (SiO_2 precursor) and initiated hydrolysis and silica condensation by addition of sodium fluoride. The microspheres were finally dried under supercritical CO_2 conditions. Synthesis of carrageenan–silica hybrid followed a similar process [06Boi]. El Kadib et al. [08Kad] impregnated chitosan beads with a titania precursor (either $Ti(aca)_2(iOPr)_2$ or $Ti(iOPr)_4$) in isopropanol solvent; after reaction, the hybrid materials were rinsed with the same solvent and finally dried under supercritical CO_2 conditions. These PNCs find extensive use as catalysts. Tsoi et al. [04Tso, 05Tso] and Brown and Rehse [07Bro] used a similar procedure for the preparation of a magnetic PSNP of alginate using $FeCl_2$ as the metal oxide precursor. Using a method termed as redox polymerization, Mallick et al. [06Mal, 08Mal] synthesized composite Cu and Pd catalysts where a monomer (o-toluidine or 5-ammo-ortho-cresol) in alcohol is mixed with Cu or Pd salts which were reduced to the zero valent metal with simultaneous polymerization of the monomer. Ponder et al. [00Pon] impregnated a hydrophobic resin with ferrous sulfate in a water/ethanol solution followed by reaction with NaOH to precipitate Hydrated ferric oxide (HFO) was reduced by $NaBH_4$ to get Fe^0 NPs within the polymer phase. He and Zhao [05Zha] used starch to synthesize bimetallic catalyst of Fe–Pd in a multistep process in which Fe^0/starch composite was prepared first using reduction of Fe(III) salts in starch followed by loading of Pd in a second step by cementation using potassium tetrachloropalladate as the precursor. Xiong et al. [07Xio] followed a similar procedure for synthesis of bimetallic NPs containing Fe^0 and other metals such as Al, Cu, Co, Ni, or Pd. Chitosan-supported magnetic Fe_3O_4 particles were synthesized by Wu et al. [09Lio, 09Wan] when chitosan was cross-linked with tripolyphosphate and was contacted with a Fe (II) precursor solution containing ferrous ammonium under controlled atmosphere (99.5 % nitrogen, 0.5 % oxygen) to carefully manage the formation of magnetic Fe_3O_4 nanoparticles within the polymer.

5.2.3 Other Methods

Other techniques have also been investigated for preparing PNCs in recent years, such as template synthesis, phase separation, self-assembly, electrospinning, etc. The template synthesis [96Cep, 96Mar, 02Fen, 10Shu], as the name suggests, uses a nanoporous material as a template to make nanoscale fillers of solid (a fibril) or hollow (a tubule) shape. The most important feature of this method may lie in that nanometer tubules and fibrils of various raw materials such as electronically conducting polymers, metals, semiconductors, and carbons can be fabricated. Cepak et al. [96Mar] prepared a semiconductor–conductor tubular nanocomposite in a 60 mm thick alumina template membrane with 200 nm diameter pores. TiO_2 tubules were synthesized within the pores of the alumina membrane via the sol–gel process before they were subjected to thermal treatment. Polypyrrole wires were then grown inside the semiconductor tubules by using the chemical polymerization method. The conductive polymer enhanced the electrical conductivity of the material, which promised a higher photoefficiency of the TiO_2–polypyrrole nanocomposites as a photocatalyst. The phase separation [07Zho] consists of dissolution, gelation, and extraction using different solvents and freezing or drying results in nanoscale porous foams. Self-assembly [01Whi, 02Hua, 10Sun] is a process in which individual, preexisting components organize themselves into desired patterns and functions. The well known self-assembly technique is the molecule-mediated one [02Hua, 10Sun] and is commonly used for construction of various nanocomposite films with desirable thicknesses. Instead of strong chemical bonds, nanoparticles are often linked by weak hydrogen bond, van der Waals, and electric/magnetic dipole interactions. Electrospinning has been widely used to produce nonwoven membranes of nanofibers [01Dei, 10Cos]. A polymer solution, such as cellulose acetate, was introduced into the electric field, and the polymer filaments were formed from the solution between two electrodes bearing electrical charges of opposite polarity. This process depends upon a number of parameters, including the type of polymers, conformation of polymer chains, viscosity of solution, polarity, surface tension of the solvents, electric field strength, and the distance between spinnerets and collectors.

5.3 Environmental Applications of PNCs

Most of the PNCs have been developed primarily in abatement of contaminants from various environmental media like groundwater or industrial effluents, gases, or soils, and the main mechanisms responsible for their environmental application are adsorption and catalytic degradation. The practical applications of these PNCs cover wide fields because the composites combine the properties of the nanoparticles and polymers. Examples of such wide range of applications in various fields include supported catalysis, sensors and biosensors for sensing and detecting pollutants particularly at trace levels, as well as for green chemistry to minimize the discharge of pollutants into the receiving environment, among various others. The following provides an account of different environmental applications of PNCs to date.

5.3.1 Adsorption of Pollutants

Adsorption techniques are widely used in water treatment and gas purification as one of the most effective and simplest approaches to removing toxic and recalcitrant pollutants. Different types of metal oxides have been dispersed within polymeric, porous host materials to develop a PNC with improved durability, robust mechanical strength, and excellent sorption characteristics. Table 1 summarizes various examples of PNC prepared and applied for sorption of different target species from the contaminated water and wastewater.

Encapsulating the metal oxide nanoparticles in a polymeric host material is necessary from the point of view of applications; however, it is also important to find out whether the functionality of the host material plays any role in the overall sorption behavior of the PNC. Theoretically, if metal oxide nanoparticles are dispersed within a cation or anion exchanger, the presence of the functional groups in the ion exchanger will influence the sorption behavior of the hybrid ion exchanger. The fixed nature of the functional groups covalently attached to the polymeric matrix of the ion exchanger makes it act like a virtual semipermeable membrane which restricts the movement of one particular type of ion across the phase boundary in an effort to conserve the electroneutrality. This gives rise to the development of Donnan potential [95Don, 10Sar]. Under the influence of this potential, groups of ions with charge similar to the functional groups (co-ions) are excluded from entering in the exchanger phase while the ions with charge opposite to the functional groups (counter-ions) tend to concentrate inside the exchanger phase. Therefore, the

Table 1 Polymer-based nanocomposites (PNCs) for adsorption of pollutants

NPs	Polymer matrix	Target pollutant	Reference
Hydrated ferric oxide (HFO)	Polymeric anion exchangers	Phosphate	[07Bla]
	Sulfonic resin	As(III), As(V)	[03Dem]
	Polymeric anion exchangers	Arsenic	[08Mol]
	Polystyrene adsorbents	Arsenic	[02Kat]
	Sulfonic resin, quaternary ammonium resin	As(III), As(V)	[05Cum]
	Polymeric anion exchangers	Arsenic	[07Syl]
	Fibrous polymeric ion exchangers	As(III), As(V)	[07Vat]
	Polyacrylamide	Pb(II), Hg(II), Cd(II)	[02Man]
	Sulfonic resin, quaternary ammonium resin	Cu(II), As(III), As(V)	[06Put]
	Purolite A-500	As(III), As(V)	[10Sar]
	Ion exchange fibers	As(III), As(V)	[06Gre]
	Polystyrene anion exchanger	As(V)	[08Zha]
Fe_3O_4	Gum arabic	Cu(II)	[07Ban]
	Chitosan	Fluoride	[07Maw]
	Alginate	As(III), As(V)	[09Esc]
	Alginate	Methylene blue, methyl orange	[08Roc]
	Cyclodextrin	Cu(II)	[11Bad]
	Synthetic resins	Cu(II)	[00Leu]
	Alginate	Cu(II)	[08Lim]
HFO + magnetite	Amberlite XAD-2	As(V), Cu(II) 2,6-dichlorophenol	[05Cu]
Iron oxyhydroxide	Cellulose	As(III), As(V)	[05Guo]
Fe (III) oxide	Alginate	Arsenic	[02Zou]
	Synthetic–COOH resin	Cd(II) Pb(II)	[00Man]
Fe(III)	Alginate	As (V)	[98Her]
Hydrous manganese oxide (HMO)	Polymeric cation exchanger	Pb(II), Cd(II), Zn(II)	[08Pan]
$SnO(OH)_2$ 1.96 H_2O	Carboxylated polyacrylamide	Pb(II), Hg(II), Cd(II)	[01Shu, 02Man]
$Zr(HPO_3S)_2$	Polymeric cation exchanger	Pb(II), Cd(II), Zn(II)	[08Zha]
Zirconium phosphate	Polymeric cation exchanger	Pb(II)	[07Pan]

ion-exchanger host material for nanoparticles of metal oxides can be made to completely reject the transition-metal cations while allowing enhanced selective sorption of anionic ligands and vice versa [06Put]. This phenomenon offers a unique opportunity to enhance the sorption properties of metal oxide nanoparticles through wise selection of the type of functional groups associated with the polymeric host. Figure 5.4a shows schematically the Donnan membrane phenomenon as applied to hybrid anion exchange resin. The concentration of anions inside the anion exchanger is much higher compared to that in the bulk. Therefore, the iron oxide nanoparticles

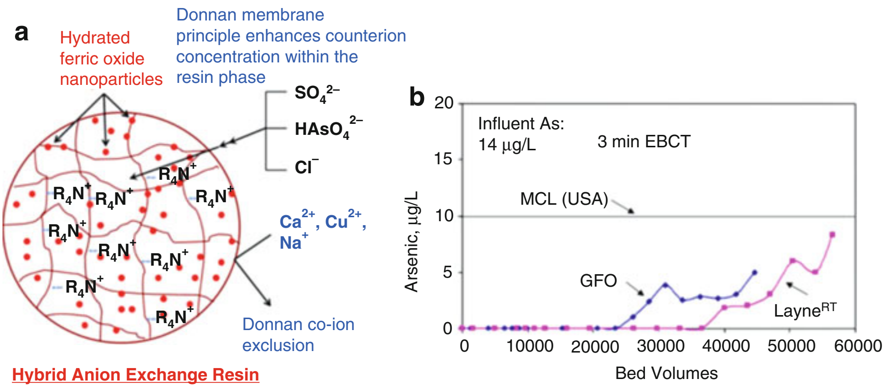

Fig. 5.4 (**a**) Schematic description of Donnan membrane principle explaining the enhanced capacity of the hybrid anion exchangers and (**b**) comparative arsenic breakthrough profiles of arsenic for field trials of hybrid anion exchanger (Layne^{RT}) and granulated ferric oxide (GFO) media

dispersed within the bead get exposed to much higher concentrations of anions and, being selective for ligands such as arsenate anions, ends up adsorbing more arsenic than iron oxide nanoparticles alone. The data shown in Fig. 5.4b from a field trial at Sahuarita, Arizona, supports this fact. Here, granular ferric oxide (GFO), an iron-oxide based adsorbent, was outperformed by a hybrid anion exchanger dispersed with Fe nanoparticles (Layne^{RT}) [11Sar].

It proves that the anion exchanger support played a critical role in enhancing the activity of the HFO nanoparticles. It is the same principle which explains the lack of arsenic removal capacity of the hybrid cation exchange resin dispersed with Fe nanoparticles as shown in Fig. 5.5.

A common cation exchanger bead contains huge number of covalently attached anionic sulfonic acid groups (on the order of 1017) [05Cum]. The negatively charged functional groups largely excluded negatively charged arsenate ions from entering the ion exchanger phase while attracting a high concentration of cations inside the resin bead. HFO nanoparticles are capable of showing amphoteric sorption behaviors at near-neutral pH adsorbing both Lewis acids and bases. The hybrid cation exchangers therefore showed high copper removal capacity while arsenic removal was absent, as demonstrated in Fig. 5.6.

Encapsulation of ferric oxide nanoparticles allow the PNC to be regenerated. In many cases, regeneration and reuse of the PNCs help improve the economics of the process, as well as in the overall ecological sustainability when the spent regenerants are transformed to innocuous end products and a small mass of contaminants that is stored in such a way not to leach any contaminant back into the environment [05Sar, 10Sar]. The adsorption capacity of the PNC was not found to deteriorate due to regeneration. It is evident from Fig. 5.6 which shows that hybrid anion exchange resins dispersed with Fe removed phosphorus with the same efficiency over a number of cycles of operation [07Bla].

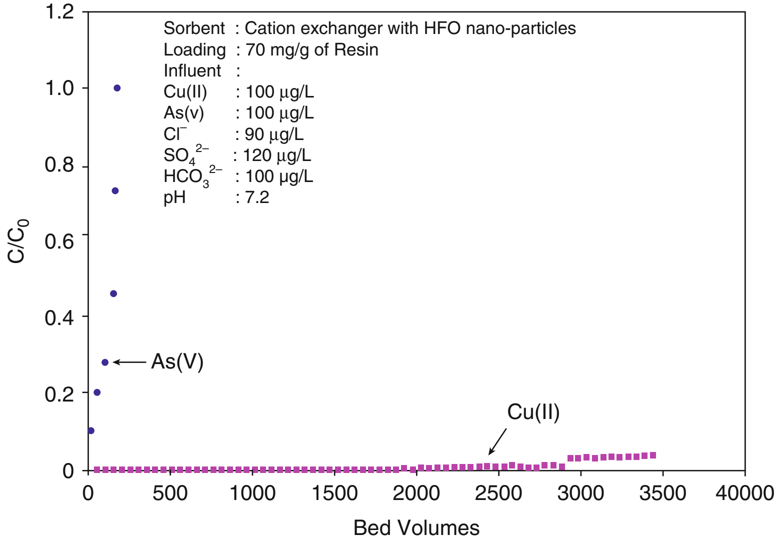

Fig. 5.5 Concentration profiles of Cu(II) and As(V) during the column run for hybrid cation exchanger dispersed with nanoparticles of hydrated ferric oxide

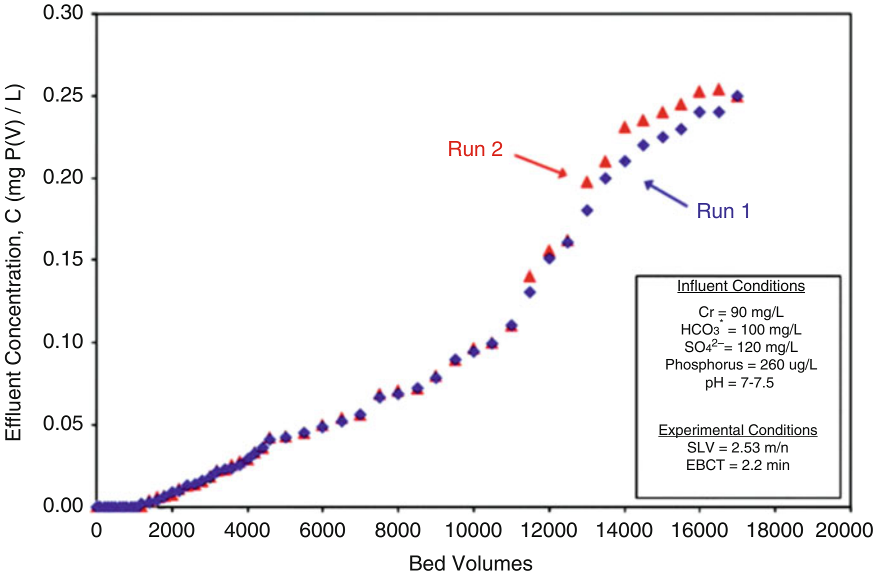

Fig. 5.6 Phosphate effluent histories during two consecutive runs with secondary wastewater from a wastewater treatment plant using “virgin” HAIX (Run 1) and “regenerated” HAIX (Run 2)

A new hybrid adsorbent HMO-001, which was fabricated by impregnating nanosized hydrous manganese dioxide (HMO) onto a porous polystyrene cation exchanger resin (D-001), provided a nice example [07Pan]. Lead adsorption onto HMO-001 was tested and the maximum capacity of HMO-001 toward lead ion was about 395 mg/g. As compared to D-001, HMO-001 exhibited highly selective lead retention from waters in the presence of competing Ca^{2+}, Mg^{2+}, and Na^{+} at much greater levels than the target toxic metal. Fixed-bed column adsorption of a simulated water indicated that lead retention on HMO-001 resulted in a conspicuous decrease of this toxic metal from 1 mg/l to below 0.01 mg/l (the drinking water standard recommended by WHO). The exhausted adsorbent particles were amenable to regeneration by the binary NaAc–HAc solution for repeated use without any noticeable capacity loss.

5.3.2 Magnetic Nanocomposites

Magnetic nanoparticles offer advantages over nonmagnetic nanoparticles because they can be easily separated from water under a magnetic field. Separation using magnetic gradients, the so-called high magnetic gradient separation (HGMS), is a process widely used in medicine and ore processing. This technique allows one to design processes where the particles not only remove compounds from water but also can be easily removed, recycled, or regenerated. Approaches have been proposed with magnetite (Fe_3O_4), maghemite (Fe_2O_3), and jacobsite ($MnFe_2O_4$) nanoparticles loading on or in the polymer matrix such as alginate beads. A series of magnetic alginate polymers were prepared and batch experiments were conducted to investigate their ability to remove heavy metal ions [08Yup, 09Liu, 11Bad] (Co (II), Cr(VI), Ni (II), Pb (II), Cu (II), Mn (II), La (III)) and organic dyes [08Roc] (methylene blue and methyl orange) from aqueous solutions. Magnetic particles in the nanocomposites allowed easy isolation of the beads from the aqueous solutions after the sorption process.

5.3.3 Catalytic and Redox Degradation of Contaminants

Nanoparticles have great potential as catalysts and redox active media due to their large specific surface area, high reactivity, and shape-dependent optical, electronic, and catalytic property, which have attracted many researchers to design highly efficient photo-/chem-catalytic materials for purification of contaminated waters and gases. The common catalytic nanoparticles include nanosized semiconductor materials (such as nano-TiO_2 [97Mil, 04Kon], ZnO [04Dan, 05Lin], CdS [98Tor, 08Dat, 09Zhu], and WO_3 [00Kwo]), zero-valence metal (such as Fe^0 [07Xio, 10Liu], Cu^0 [05Lin, 09Wu] and Zn^0 [08Son, 08Wan]), and bimetallic nanoparticles (such as Fe/Pd [98Zha, 01Ell, 05Guc, 08Wan], Fe/Ni [02Sch, 07Bar], Fe/Al

Table 2 Several polymer-based nanocomposites (PNCs) for degradation of pollutants

NPs	Polymer matrix	Target pollutant/reaction	Reference
TiO_2	Polyhydroxybutyrate (PHB)	Methylene blue	[06Yew]
	Polyaniline (PANI)	Phenol	[11Wan]
	Poly(3-hexylthiophene) (P3HT)	Methyl orange	[09Zha]
	Poly(tetrafluoroethylene)	Trichlorobenzene	[98Uch]
	Polyethylene (PE)	Methylene blue	[98Nas]
	Nafion	Victoria Blue R	[10Che]
SiO_2	Chitosan	Monoglyceride synthesis	[04Mol]
CdS	Chitosan	Congo red	[09Zhu]
Fe^0	Alginate	Trichloroethylene	[07Kim]
	Chitosan	Cr(VI)	[10Liu]
	Resin	Cr(VI) and Pb(II)	[00Pon]
Cu^0	Resin	Carbon tetrachloride	[05Lin]
	Chitosan	Cr(VI)	[09Lio]
Cu_2^0	Chitosan	Dye photodegradation	[08Li]
Pd^0	Chitosan	Hydrogenation of nitro compounds	[04Gui]
			[03Vin]

[08Che], Zn/Pd [09Riv]). They usually serve as catalysts or redox reagents for degradation of a large variety of environmental contaminants such as PCBs (polychlorinated biphenyls) [07Var, 10Liu], azo dyes [04Dan, 04Kon, 09Zhu], halogenated aliphatics [07Xio, 08Son], organochlorine pesticides [09Wu, 08Son], halogenated herbicides, and nitroaromatics [01Kon, 08Dat]. However, the use of aqueous suspensions limits their wide applications because of the problems concerning separation of the fine particles and the recycling of the catalyst. Immobilization of these nanoparticles onto polymer matrix such as porous resins [01Pon, 05Lin, 09Lin], ion exchangers [08Kim], and polymeric membranes [03Ike] has been available to solve the problems to considerable extent, serving for the reduction of particle loss, prevention of particles agglomeration, and potential application of convective flow occurring by freestanding particles. Table 2 summarizes some PNCs reported recently for catalytic removal of pollutants from different environmental media.

Bio- and synthetic polymer–nanoparticle composites have been extensively studied during the last decades as support for heterogeneous catalysis. A wide range of reactions have been investigated, including oxidation, hydrogenation, cyclic polymerization, Suzuki cross-coupling reaction, Tsuji–Trost reaction, and so on. A review on chitosan as support for heterogeneous catalysis has been published by Guibal (2005) [05Gui]. Apart from the functionality of the polymer matrix, it is also important to consider the physical properties and the final application of the PNC. The parent polymer as well as the synthesized PNC must provide sufficient permeability for the target ions or molecules or reactants to gain access to the nanoparticles which actually is the site where the catalysis reaction takes place. Thus, for the reactions taking place in aqueous phase or in polar solvents, the polymer must be hydrophilic or swell slightly in water to enhance the desired properties.

As for the widely used catalyst nano-TiO_2, they have been extensively studied for degradation of organic pollutants [97Mil, 04Kon]. Illumination promotes an electron to the conduction band, leaving a hole in the valence band. This process produces a potential reducing and oxidizing agent. Because of the high photocatalytic activity of titanium dioxide nanoparticles, the polymer substrates of the nanocomposite catalysts are expected to be antioxidative under UV or visible light illumination. Reported polymeric substrates were usually saturated carbon chain polymers or fluoropolymers, such as poly(dimethylsiloxane) (PDMS) [03Ike], polyvinyl pyrrolidone (PVP) [10Wan], polyethylene (PE) [98Nas], polypropylene (PP) [96Ten], poly(3-hexylthiophene) (P3HT) [09Zha], polyaniline (PANI) [11Wan], poly(tetrafluoroethylene) [98Uch], and Nafion [10Che]. Ameen et al. prepared poly 1-naphthylamine (PNA)/TiO_2 nanocomposite by in situ polymerization and observed an enhanced photocatalytic activity for the degradation of methylene blue (MB) dye under visible light illumination. The high photodegradation efficacy of the MB dye may be attributed to the efficient charge separation of the electrons (e^-) and hole (h^+) pairs at the interfaces of PNA and TiO_2, as suggested related to the slightly high red shift in UV–Vis results.

Laboratory research has established that some nanoscale metals and bimetals such as Fe^0, Cu^0, Zn^0, Fe/Pd, Fe/Ni, Pd/Zn, etc., are very effective in destroying various organic contaminants [00Pon, 01Ell, 02Sch, 05Lin, 06Guo, 07Bar, 07Xio, 08Che, 08Son, 08Wan, 08Wan, 10Liu] such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes. The reactivity of these metal nanoparticles is usually very high, for example, nZVI can even self-ignite when exposed to air. Thus, supporting the particles is requisite to preserve their chemical nature by inhibiting oxidation until they can react with the targeted pollutants. Lin et al. [05Lin] ever synthesized nanoscale zero valent copper (nZVC) supported on a cation exchange resin to enhance the removal of carbon tetrachloride (CCl_4) from water (Fig. 5.7). The use of the cation exchange resin as a support effectively prevented the reduction of surface area due to the agglomeration of nZVC particles. Moreover, the cation exchange resin recycled the copper ions produced from the reaction between CCl_4 and Cu^0 by simultaneous ion exchange. The decline in the amount of CCl_4 in aqueous solution resulted from the combined effects of degradation by nZVC and sorption by the host resin. The pseudo-first-order rate constant normalized by the surface-area and the mass concentration of nZVC was approximately 20 times that of commercial powdered ZVC. He et al. reported a composite of parallelized iron (Fe/Pd) nanoparticles with sodium carboxymethyl cellulose (CMC) as a stabilizer. Compared to pristine Fe/Pd particles, the CMC-stabilized nanoparticles displayed markedly improved stability against aggregation, chemical reactivity, and soil transport. Batch dechlorination tests demonstrated that the CMC-stabilized nanoparticles degraded trichloroethene (TCE) 17 times faster than their nonstabilized counterparts based on the initial pseudo-first-order rate constant.

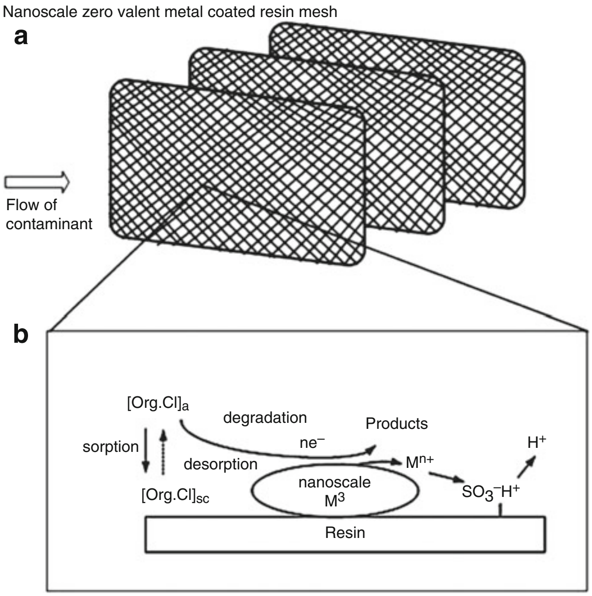

Fig. 5.7 Application of nanoscale zerovalent copper coated resin mesh in an aboveground reactor and the associated reactions [05Lin]

5.3.4 Biocatalytic Nanocomposites

Biocatalysts such as enzymes or catalytic antibodies are natural nanoreactors regulated by biochemical factors in the microenvironment of living cells. Their high specificity and targeted effectiveness as well as environmental benignancy render them to be a more attractive choice than synthetic catalysts for pollutant degradation. However, the relatively short lifetime of enzymes and their sensibility greatly dependent upon environmental conditions (pH, temperature, mechanical stress, etc.) tend to limit their industrial application. Improvement in enzyme stability became important for practical applications because it can subsequently reduce the amount of enzyme required, prolong the lifetime of enzymes, and increase the potential for the reuse of enzyme.

Researchers have experimented with various methods such as immobilization, modification, and genetic modification for the improvement in enzyme stability, in which enzyme immobilization appeared to be one of the most successful approaches. Natural and synthetic polymers [96Sil, 05Sha, 06Jor, 07Tri, 09Chi] (polysaccharides, polyacrylamides, alginates, resins, chitosan, etc.) have been used for bio-immobilization via loading or entrapment. For example, Amberlite MB 150 and chitosan beads were used by Tripathi et al. [07Tri] to immobilize α-Amylase from mung beans (*Vigna radiata*). The performance of free and immobilized enzymes was compared. The activity loss for free amylase after 100 days of storage at 4 °C was ~70 %, whereas for Amberlite- and chitosan-based amylases it was 45 % and 55 %, respectively, under the identical experimental conditions. Moreover, polymer-based amylase showed a residual activity of 43 % and 27 %, respectively, after 10 uses.

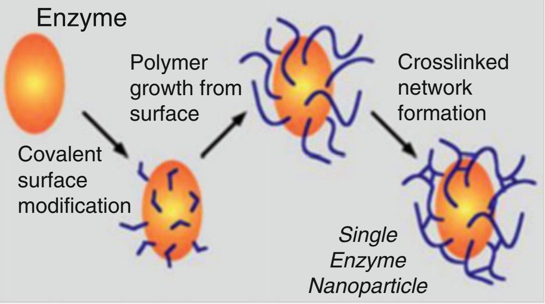

Fig. 5.8 Diagram of a typical modification process for creating SENs

Enzyme entrapment protects enzymes by preventing their direct contact with the environment, thereby minimizing the effects of gas bubbles, mechanical sheer, and hydrophobic solvents. Nevertheless, there still exist some drawbacks such as mass transfer limitations and low enzyme loading. Recently, a new method of enzyme stabilization has been reported under the name single-enzyme nanoparticles (SENs) [03Kim, 06Kim, 08Yan], in which each enzyme molecule was surrounded with a porous composite organic/inorganic network of less than a few nanometers in thickness (as illustrated in Fig. 5.8). Two tested proteases (α-chymotrypsin and trypsin) [03Kim] were significantly stabilized and kinetic studies with the SENs of chymotrypsin revealed that there was no serious mass transfer limitation on the substrate.

5.3.5 Green Chemistry

Pollution prevention by nanotechnology refers, on one hand, to a reduction in the use of raw materials, water, or other resources and waste reduction or elimination, and on the other hand, to more efficient use of energy or involvement in energy production. Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [02Bre]. Nanomaterials can play a key role in the green chemistry process by minimizing the use of toxic chemicals, solvents, and energy, and PNCs fall within the scope of such functional materials. Table 3 illustrates some typical applications of PNCs in these fields.

For one thing, polymer-based nanocatalysts can make chemical manufacturing more efficient and more environmentally benign by providing higher selectivity for desired reaction products, helping to eliminate wasteful secondary reactions and reduce energy consumption [99Lu, 04Pra, 08Sar]. For example, polymer-protected bimetallic alloy nanocluster was widely used as a catalyst to control the activity, selectivity, and stability of certain reactions, which is expected to minimize the consumption of chemical reagents and production of hazardous substances [99Lu]. Besides, some nanocatalysts functioning at room temperature open the way for broad applications of nanomaterials in many consumer products.

For another thing, polymers loaded with nanoparticles could also be used as benign alternatives for harmful materials, reducing the energy requirement and waste generation [06Kim, 06Yew, 08Kim, 09Buz]. Photocatalytic nanoparticles like

Table 3 Polymer-based nanocomposites (PNCs) for green chemistry

Type	NPs	Polymer matrix	Preparation method	Reference
Ecofriendly materials	TiO_2	Polyhydroxybutyrate (PHB)	Solvent-cast	[06Yew]
	TiO_2	Hyperbranched poly (ε-caprolactone) (HPCL)	Dip-coating	[08Kim] [06Kim]
Polymer-based nanocatalysts	Cu^0	Poly(N-vinyl-2-pyrrolidone) (PVP)	In situ synthesis with Cu(II) as Precursor	[08Sar]
	Au^0	Anion exchanger	Mixing	[04Pra]
	Ni/Pd	Poly(N-vinyl-2-pyrrolidone)	Polyol reduction	[99Lu]
Energy storage	TiO_2	Sulfonated poly(ether ether ketone) (SPEEK)	Solvent-cast	[07Kal]
	Phosphorylated titanate	Chitosan	Solvent-cast	[10Wan]

titanium dioxide have been widely used to produce photodegradable polymers, which helps to reduce emission of toxic by-products during polymer incineration. Kim et al. demonstrated suppression of dioxin emission for poly(vinyl chloride) (PVC) incineration when titanium dioxide (TiO_2) nanocomposites were employed [08Kim]. The GC (gas chromatography) results on the exhaust gases from incineration showed that the emissions of dioxin and precursors were largely suppressed with the increasing content of TiO_2 in PVC/TiO_2 nanocomposite, as compared with those in the neat PVC without TiO_2.

In addition, PNCs may also be applied in energy production and storage. One example is the utilization of PNCs in direct methanol fuel cells (DMFC) [07Kal]. With characteristics such as low working temperature, high energy-conversion efficiency, and low emission of pollutants, DMFCs may help solve the future energy crisis. However, an obvious limitation to DMFC is the slow reaction kinetics, which reduces the power output. Catalysts composed of metal or metal oxide nanoparticles, supported on conducting polymers, are adopted to be an effective approach. Rhee et al. [06Rhe] reported that the membrane electrode assembly using Nafion/sulfonated titanate nanocomposite membranes exhibited up to 57 % higher power density than the assembly containing a pristine Nafion membrane under typical operating conditions of DMFC.

5.4 Pollutant Sensing and Detection

Rapid and precise sensors capable of detecting pollutants at molecular levels could enhance our understanding and protecting the environment. Manufacturing, process control, compliance, ecosystem monitoring, and environmental decision making would also be significantly improved if more sensitive and less costly techniques for contaminant detection were available. Actually, nanoparticles are receiving growing attention for pollutants detection owing to their specific characteristics of large specific surface area and good biocompatibility. As a large fraction of the atoms are present at the surface in nanosized materials, the surface properties such as the depth of the surface space charge region become pivotal. When the particle size gets into nano range, the coating layer takes over the bulk, and it becomes difficult to distinguish surface from bulk conduction [00Cra]. These characteristics of nanosized particle make the materials particularly appealing in applications of sensors [01Tse]. Nevertheless, the drawback of nanoparticles in practical application such as slow diffusion and aggregation still exists. Immobilization of nanoparticles by polymer matrix is one of the most efficient approaches to overcome such shortcomings. Since the chemical and physical properties of polymers may be tailored, they gained importance in the construction of sensor devices [04Adh]. Conductive polymer nanomaterials have attracted particular interests as sensors for air-borne volatiles [02Sur, 04Jia, 05Sug] (alcohols, NH_3, NO_2, CO) because of large surface area, adjustable transport properties and chemical specificities, easy processing, and scalable productions. Polythiophene based sensor has shown the detection of hydrazine gases at ppb levels [06Gee]. Also, polyaniline-SnO_2/TiO_2 nanocomposite ultrathin films have been fabricated for CO gas sensing [185]. The range of the biosensor was found to be $6.9 \times 10^{-14}$to 8.6×10^{-13}mol/l and the detection limit is 2.3×10^{-14}mol/l. A Pd–polyaniline nanocomposite was developed as a selective methanol sensor [06Ath]. The synthesized nanocomposite sensor showed high selectivity and sensitivity to methanol vapors with rapid and reverse response. Some applications of PNCs as various sensors are included in Table 4.

5.4.1 Biosensor

The total effect of a biosensor is to transform a biological event into an electrical signal, as illustrated in Fig. 5.9. Biosensors have found extensive applications in environmental pollution control for measuring toxic gases in the atmosphere and toxic soluble compounds in waters. By far the largest group of direct electron transfer biosensors is based on co-immobilization of the enzyme in a conducting polymer, namely polypyrrole [91Kaj] and polyaniline [06Sin]. For example, a cholesterol biosensor was fabricated by co-immobilize cholesterol oxidase, cholesterol esterase, and peroxidize onto electrochemically prepared polyaniline films [06Sin]. This polyaniline-based cholesterol biosensor has a response time of about 240 s, an apparent K_m value as 75 mg/dl, and can be used to estimate cholesterol concentration up to 500 mg/dl. These polyaniline/cholesterol oxidase/cholesterol esterase films have a detection limit of 25 mg/dl with sensitivity of 0.042 μA mg/dl. The enzyme films were found to be thermally stable up to 48 °C and have a shelf-life of about 6 weeks when stored at 4 °C.

Table 4 Polymer-based nanocomposites (PNCs) for pollutant sensing and detection

Sensor type	NPs	Polymer matrix	Preparation method	Detection target	Reference
Gas sensor	SnO_2	Polystyrene/ polyaniline (PSS/PANI)	In situ self-assembly	CO	[05Ram]
	SnO_2	Polyaniline (PANI)	Hydrothermal method	Ethanol, acetone	[07Gen]
	TiO_2	Polyaniline (PANI)	Chemical polymerization and a sol–gel method	Trimethylamine	[08Zhe]
	Iron Oxide	Polypyrrole	Simultaneous gelation and polymerization	CO_2, N_2, CH_4	[02Sur]
	Pd	Polyaniline	Oxidative Polymerization of solution with Pd NPs	Methanol	[06Ath]
Biosensor	Au	Chitosan	One-step electrodeposition	Glucose	[04Luo]
Chemical sensor	Au	Chitosan	Mix in solution	Zn^{2+}, Cu^{2+}	[05Sug]
Humidity sensor	TiO_2	Polypyrrole	In situ photopolymerization	Change in humidity	[07Su]

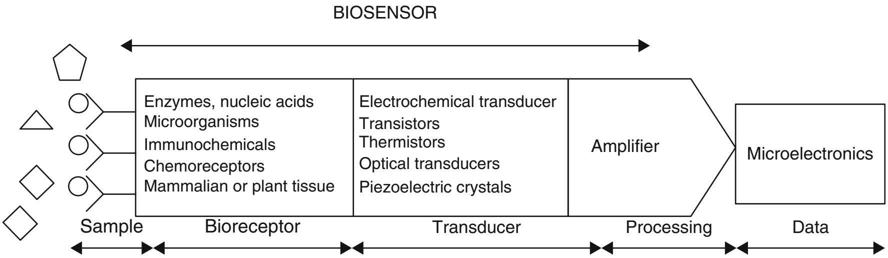

Fig. 5.9 Major stages of measurements of analytes with a biosensor [04Adh]

5.5 Conclusion

The environmental applications of PNCs are interesting and endless. The widespread use of PNCs in adsorption of pollutants, photo-/chem-catalysis degradation, and pollutant sensing and detection result in less pollution and benign products. Till now numerous PNCs are available for environmental purpose, and currently fabrication of new PNCs of high efficiency and low cost is still a hot topics. Also, we hope the polymeric hosts are available through cleaner processes instead of environmental unfriendly ones. In addition, further insights into the interplay between the host polymers and the encapsulated NPs are still required. For example, how does the polymer chemistry affect the dispersion and distribution of NPs? What is the effect of the immobilized NPs on the properties of the resultant PNCs such as mechanical performances? Certainly, the interaction between PNCs and the targeted pollutants or the substrates should be further revealed, and modern analytical tools like XAS (x-ray absorption spectroscopy) and AFM may help us to deeply understand the underlying mechanism at micro scale levels. Besides, most of the recent achievements are still based on laboratory-level tests. Many issues may need to be solved in the mass production and field application.

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Polymer Nanocomposites for Energy and Fuel Cell Applications

6

Ananta Kumar Mishra and Mayur C. Valodkar

6.1 Introduction

Energy has become the primary focus of major world powers and scientific community due to the dependency of the technological advancement, depletion of fossil fuel, and increasing pollution. Hence, there is an urgent need for the development of clean, efficient, and sustainable energy source. The most effective technologies developed for the electrochemical energy conversion and storage are fuel cells (FCs) [00Geb, 11Bos, 12Mis], solar cells [11Che, 12Mis, 12Zha], lithium-ion battery (LIB) [06Ste, 08Li, 09Cai], and supercapacitors (SCs) [12Bos, 12Tiw, 12Yi]. There are several aspects and components which govern the efficiencies of the aforementioned technologies. However, encasing all these aspects is beyond the scope of this chapter, and this chapter will highlight the importance of clay and carbon-based polymer nanocomposites for these applications.

6.1.1 Fuel Cells

Fuel cells have the merit of converting chemical energy into electrical energy. Among the several varieties of available fuel cells (solid oxide fuel cell, molten carbonate fuel cell, alkaline fuel cell, polymer electrolyte membrane fuel cell (PEMFC), and direct methanol fuel cell (DMFC)), polymer membranes are being used only in PEMFC and DMFC. The schematic depiction of PEMFC and DMFC is shown in Fig. 6.1. Both PEMFC and DMFC are comprised of an anode and a cathode separated by a proton-conducting polymer membrane. The fuel (hydrogen

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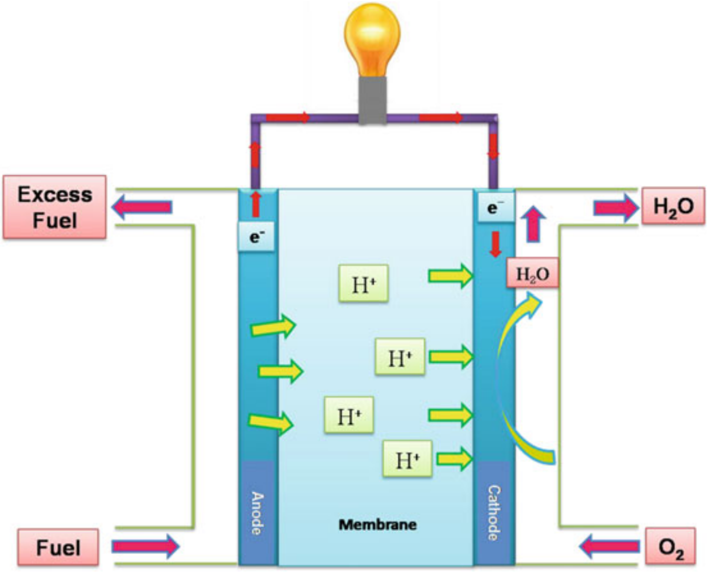


Fig. 6.1 Schematic depiction of PEMFC and DMFC.

in case of PEMFC and methanol in case of DMFC) gets dissociated at the catalyst layer present in the anode. This generates proton and electron at the anode. The proton passes through the polymer membrane, whereas the electron is being dragged through an external electrical circuit. The proton and the electron combine with the reduced oxygen at the cathode surface and generate water. The electron transmitted through the external electrical circuit generates electricity.

The mechanisms of proton generation at the anode surface are different for both PEMFC and DMFC and are shown in Eqs. 6.1 and 6.2, respectively. However, the mechanism for the water generation at the cathode surface is similar for both PEMFC and DMFC (Eq. 6.3).

$$H_2 \rightarrow H^+ + e^- \tag{6.1}$$

$$2CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \tag{6.2}$$

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O + \text{Energy} \tag{6.3}$$

The objective of the polymer membrane in PEMFCs and DMFCs is to provide a path for proton conduction from anode to cathode, and, hence, a limited number of membranes are suitable for this application. The membranes also face harsh environment during the energy conversion process. Hence, the main requirements of polymer membranes suitable for fuel cell applications are excellent proton conductivity, good electrical insulation, high thermomechanical and chemical stability, cost-effectiveness, good barrier property, low swelling stresses, and capability for membrane electrode assembly fabrication [11Bos, 12Mis].

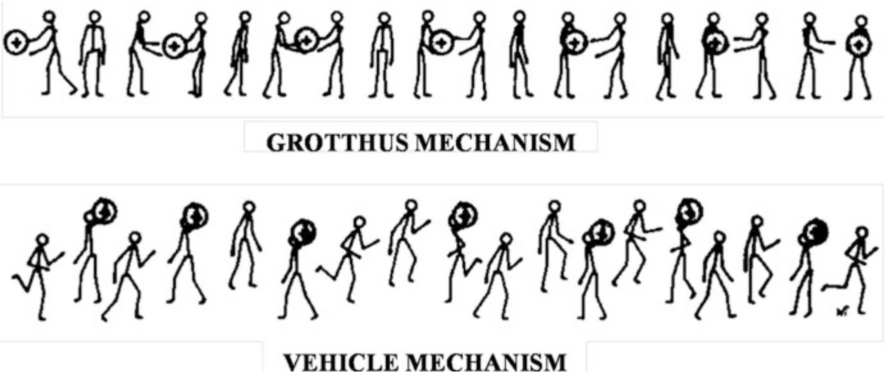


Fig. 6.2 Mechanism of proton transportation in polymer membrane (Ref. [88Kre])

6.1.1.1 Proton Conduction Mechanism

The proton conduction through a polymer membrane occurs via two types of mechanisms, namely, vehicle and Grotthus mechanism. The proton requires a carrier/vehicle in vehicle mechanism, whereas it moves from the anode to the cathode through a network of hydrogen bond in Grotthus mechanism. Figure 6.2 shows the artistic presentation of the two mechanisms as proposed by Kreuer [88Kre]. The presence of organic groups such as $-SO_3H$ $-HPO_4$, solid acids, moisture, etc. in a polymeric membrane can be beneficial for proton transport in the membrane. Several polymers such as Nafion, sulfonated polyarylenes (including sulfonated polyether ether ketone (SPEEK), sulfonated polyimide (SPI), sulfonated polyether sulfone (SPES), etc.), and phosphoric acid-doped polybenzimidazole (PBI)-type membranes have also been developed in the due course. However, the membranes developed so far are yet to meet the department of energy (DOE) targets. Despite the fact that Nafion is the most widely accepted membrane for fuel cell, the high membrane cost, permeability toward fuel, and its inferior proton conductivity at high temperature and low humidity limit its end application. Hence, efforts have been made to develop new varieties of membranes and techniques to meet the DOE targets.

6.1.1.2 Proton Transport in Nafion

The drastic change in proton conductivity of Nafion above certain temperature and low humidity conditions raised questions about the proton transport mechanism in Nafion and is beneficial for designing new membranes. Nafion consists of a hydrophobic perfluorinated backbone which is responsible for its mechanical strength, and the hydrophilic sulfonic acid group provides the path for proton conduction. Solid-state nuclear magnetic resonance and small-angle X-ray scattering studies have revealed the presence of interconnected ion channels in Nafion at 100 % relative humidity (RH) due to the self-organization of highly hydrophilic $-SO_3H$ group and C-F backbone upon hydration. The interconnected ion channels provide paths for

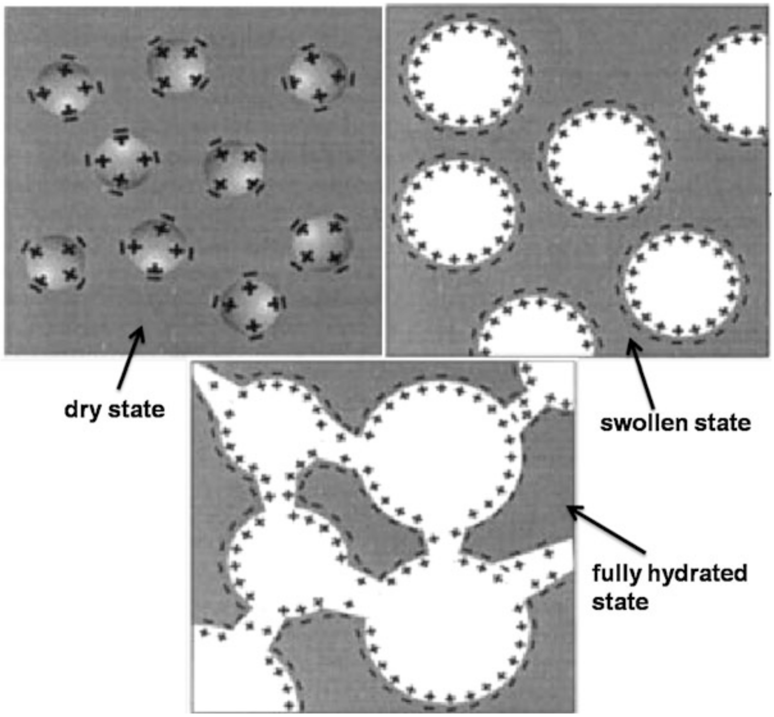


Fig. 6.3 Humidity-dependent swelling of Nafion membrane (Ref. [00Geb])

proton migration from anode to cathode via Nafion membrane. These interconnected ion channels shrinks at low humidity and above 80 °C which is responsible for the drastic decrease in ion conductivity above certain temperature and humidity conditions [11Bos, 12Mis]. The humidity-dependent swelling of Nafion is shown in Fig. 6.3 [00Geb].

6.1.1.3 Organic-Inorganic Hybrid Membranes

The demerits associated with Nafion and other membranes have escorted to the development of new techniques of membrane preparation including the development of organic-inorganic hybrid membranes, polymer blending, and sulfonation of the membranes. Preparations of organic-inorganic hybrid membranes have attracted many researchers due to their manifold benefits to the membranes. Inorganic nanofillers are well known for their reinforcing nature upon incorporation to the organic polymers leading toward the enhancement in mechanical properties of the nanocomposites. The hydrophilic nature and water retention capability of the nanofillers are the added advantages for their applications in PEMFCs and DMFCs. Hence, several nanofillers including clay, silica, TiO_2, carbon nanotube (CNT), graphene oxide (GO), etc. have been incorporated in polymer membranes. Addition of inorganic nanofillers into polymer membranes improves the operating temperature of the fuel cell, barrier toward fuels, and the thermomechanical properties. Despite the application of several inorganic nanofillers for the fabrication of polymer nanocomposite membranes, the current chapter will cover only the use of clay and carbon-based nanofillers for the fabrication of nanocomposites membranes. Surfaces of the nanoclays and carbon-based fillers are modified with organic modifiers to enhance the degree of dispersion and polymer-filler interaction.

Surface Modifications of Nanofillers

Two varieties of nanoclays, namely, montmorillonite (MMT) and Laponite (synthetic hectorite clay), are being used for the fabrication of polymer nanocomposite membranes. Surfaces of the nanoclays are modified by ionic, covalent, or plasma modification techniques taking into account the presence of replaceable Na^+ ions in the interlayer gallery spacing and the –OH groups present on the edges of the nanoclays, respectively [07Zha, 10Buq]. Ionic modifications of nanoclays are performed in two ways (e.g., acid activation and ion exchange with alkyl ammonium ions) by the replacement of exchangeable Na^+ ions present in the interlayer gallery spacing of nanoclays. The covalent modification of nanoclays involves the reaction between the –OH groups present on the surface of the nanoclays with alkyl silanes. However, for plasma treatment, the modifiers endcapped with vinyl groups are covalently attached to the clay surface. In most of the cases, surface modifiers containing $–SO_3H$ and $–PO_3H$ groups are being used to further enhance the proton-conducting nature of nanoclays. Mishra et al. have reported the presence of H_3PO_4 on the surface of Laponite XLS (peptized version of Laponite). These H_3PO_4 are generated in situ due to the hydrolysis of peptizer ($Na_4P_2O_7$) adsorbed on the surface of the clay during its acid activation (Fig. 6.4) [12Mis].

As described earlier, polymer membranes should be electrically insulating in nature to avoid short circuit between the anode and the cathode. However, most of the carbon-based nanofillers have good electrical conductivity which may increase the electrical conductivity of the respective nanocomposite membranes. Hence, the surfaces of the CNTs were functionalized with modifiers containing $–SO_3H$ and $–PO_3H_2$ groups prior to incorporating into the polymer matrices [08Kan, 10Kan, 11Zho]. Graphene oxide prepared by modified Hummers method was used without further modification owing to their low electrical conductivities due to the presence of oxygen functionality on their surfaces [11Zar, 13Kui].

Membrane Fabrication

The clay- and carbon-based nanocomposite membranes are generally prepared by solvent casting technique. Different types of solvents such as a mixture of ethanol and water, dimethylformamide, dimethylacetamide or N-methylpyrolidone, etc. have been chosen for the preparation of nanocomposite membranes depending on the types of polymer and dispersibility of the fillers.

Physical Properties of the Hybrid Membranes

Proton conductivity and cell performance of the membranes at desired temperature and humidity are important for the end applications of the membranes. However, the

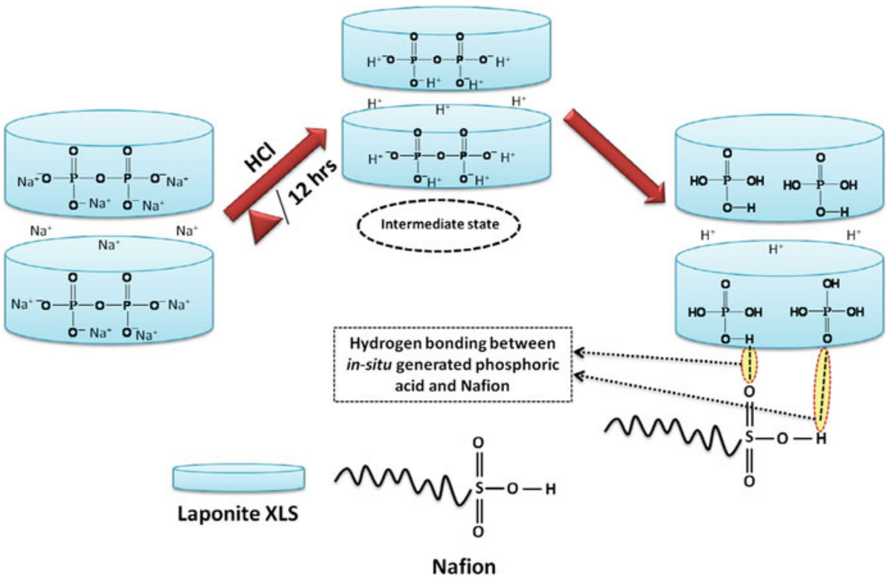


Fig. 6.4 Acid activation of Laponite RDS using HCl (Ref. [12Mis])

membranes should be stable enough to resist the hoarse thermal and chemical environment for their long-term durability. Hence, measurements of their thermomechanical properties are also important. The water uptake and retention behavior of the membranes provides added advantage to the proton conductivity and performances of the membranes.

Mechanical and Dynamic Mechanical Properties of the Membranes

The reinforcing nature of nanofillers (both nanoclays and carbon-based nanomaterials) renders an increase in the tensile strength (TS) and modulus of the nanocomposites compared to their respective parent polymers (Fig. 6.5), provided the nanomaterials are well dispersed in the polymer matrix [10Swa, 11Xin, 12Mis]. It is further evident from the 160 % increase in the Young's modulus of the Nafion-CNT composite compared to the pure Nafion [07Tho]. "The decrement or increment in elongations at break of the nanocomposite membranes compared to pure membrane is not consistent and depends on several factors (such as types of nanofillers and their degree of dispersion" [04Son, 06Tho, 07Tho, 08Cho]. The mechanical properties of the nanocomposites increase with increasing nanofiller content up to certain amount beyond which it deteriorates (Fig. 6.6) due to the dominance of filler-filler interaction compared to polymer-filler interaction leading to inferior nanofiller dispersion in the polymer matrix [06Tho, 12Kum].

Thermal Stability

As described earlier, membranes have to pass through hoarse environment in practical applications, and thermal stability of the membranes should be high enough

Fig. 6.5 Change in the storage modulus of nanocomposites with respect to temperature (Ref. [12Mis])

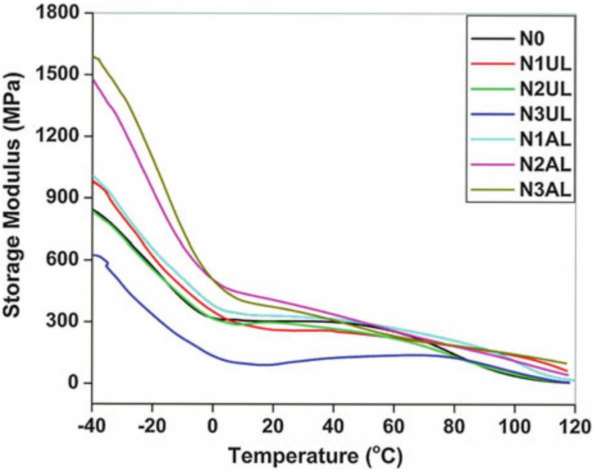
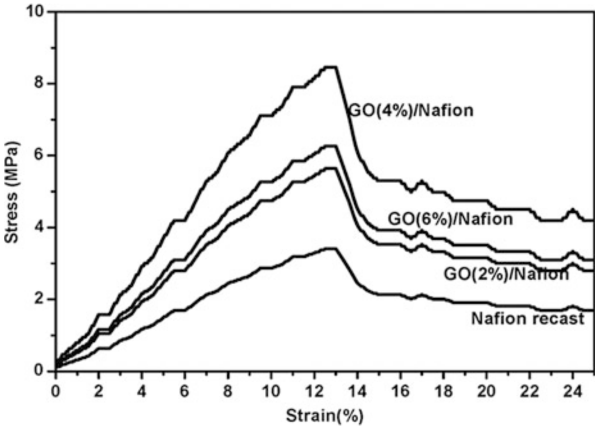
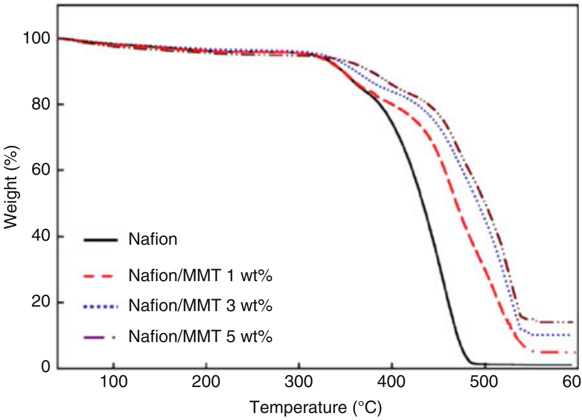


Fig. 6.6 Stress versus strain curves of GO/Nafion composites and recast Nafion membranes (Ref. [12Kum])



for their durability. Nafion shows three stages of degradation under nitrogen atmosphere. The weight loss up to 300 °C corresponds to the loss of water molecules. The sulfonic acid groups and the teflonic polymer backbone start degrading at 350 and 400 °C, respectively [09Gna]. Addition of modified MMT to Nafion membrane has increased the weight loss of the nanocomposites due to the degradation of –SO_3H group present in both the modifier and the Nafion but enhanced the thermal stability of the teflonic backbone compared to the virgin Nafion [04Son, 07Zha] (Fig. 6.7). The degradation of other sulfonated polymer membranes (sulfonated polyarylenes) also commences at nearly 300–400 °C due to the loss of –SO_3H groups. Well-dispersed nanofillers in the entire polymer membranes not only enhance the polymer-filler interaction but also improve the thermal stability of the nanocomposites. This is due to the fact that the nanodispersed fillers prevent faster heat transmission through the membrane [03Cha, 06Son, 06Tho, 10Swa, 11Doğ].

Fig. 6.7 Thermal stability of Nafion-clay nanocomposite membranes (Ref. [04Son])



Water Uptake

The presence of water or moisture in the membrane allows easier proton transportation within the membrane. Hence, water uptake and water retention capability of membranes are important parameters for their suitability in PEMFC applications. The water uptake of the membranes can be calculated using the following equation:

$$Water\ uptake = \frac{W_t - W_d}{W_d} \times 100 \tag{6.4}$$

where W_d is the dry weight of the membrane and W_t is the weight of the membrane after swelling at a particular temperature for 24 h.

The water uptakes of the membranes are highly dependent on temperature, and hence, it is necessary to mention the measurement temperature along with the water uptake values. The presence of the hydrophilic –SO_3H groups provides water uptake of ~33 % to Nafion, and the water uptake increases with increasing temperature. Incorporation of nanoclays to Nafion matrix enhances the water uptake of the composite membranes due to the hydrophilic nature of the nanoclays which increases further with the amount of nanoclay in Nafion matrix [08Xiu, 10Kim]. In the case of sulfonated polyarylenes, water uptake is highly dependent on the degree of sulfonation (DS) due to the increased hydrophilic –SO_3H groups with increasing DS. SPEEK membranes with DS of 69.4 and 85 % have shown water uptakes of ~42 and 91 %, respectively [10Rei]. Hydrophilic and hydrophobic modifiers to the nanoclay also play a role in the water uptake of the nanocomposite membranes. Nanoclays modified with alkyl ammonium groups containing highly hydrophilic moieties like –SO_3H help in improving the water uptake of the membranes, whereas hydrophobic modifier such as dimethyl dioctadecylammonium chloride (DMDOC) reduces the water uptake of the nanocomposites [06Son, 11Doğ]. Compared to all other factors described earlier, the degree of clay dispersion in the polymer matrix plays more significant role in determining the water uptake of the nanocomposite membranes irrespective of the types of modifier and polymer.

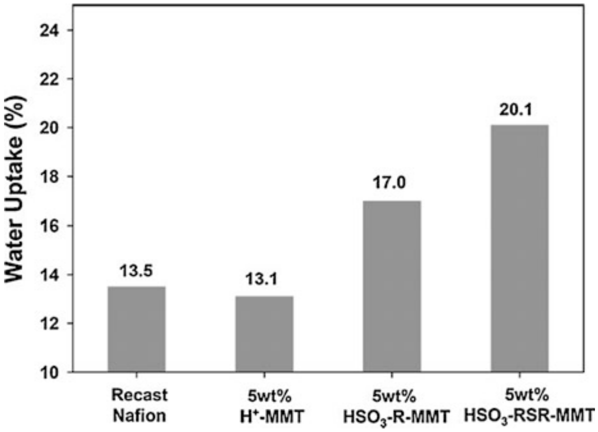


Fig. 6.8 Water uptakes of Nafion-clay nanocomposite membranes (Ref. [10Kim])

The presence of highly aggregated structure of the nanoclays in the polymer membranes can reduce the water uptake of the nanocomposites, and it can even be lower than the virgin membranes. This is ascribed to the reduced exposed outer surface area of the aggregated nanoclays [06Son, 10Kim] (Fig. 6.8).

GO is highly hydrophilic in nature, and its colloidal solution in water is stable for months due to the presence of oxygen functionalities such as epoxy, hydroxyl, and carboxylic groups [13Kui]. Hence, well-dispersed GO in the polymer membrane enhances the water uptake of the membrane, but reverse trend can be seen with aggregated GO [11Zar, 12Kum]. Similar trend can also be seen with CNT-based nanocomposite membranes.

Proton Conductivity

Reliable proton conductivity is the most important aspect of polymer membranes suitable for PEMFC applications. In its fully swollen state (or 100 % RH), the proton conductivity of Nafion varies from 0.07 to 0.1 S cm^{-1} depending on the membrane preparation process. Nanoclays are expected to enhance the proton conductivities of the nanocomposite membrane due to their hydrophilic nature. However, the results obtained are not consistent with the aforementioned proposition, and several other factors such as degree of dispersion and types of surface modifier contribute to the proton conductivity of the nanocomposite membranes. Increase in water uptake also does not confer a similar increase in the proton conductivity of the membranes.

A comparative study on the effect of the modifier to the clay containing different counterions (H^+, Na^+, and ammonium counterions) toward the proton conductivity of the Nafion-clay nanocomposite shows the highest conductivity for the nanocomposite comprising of nanoclay with H^+ counterion compared to the other two varieties of nanoclays due to the easier mobility of H^+ ion [04Tho] (Fig. 6.9). The acid-activated Laponite XLS clay has also resulted in a significant increase in the proton conductivity of the Nafion-clay nanocomposite due to the presence of highly conducting in situ generated H_3PO_4 on the nanoclays. The highest proton conductivity of 0.27 S cm^{-1} has been noted with nanocomposite containing merely

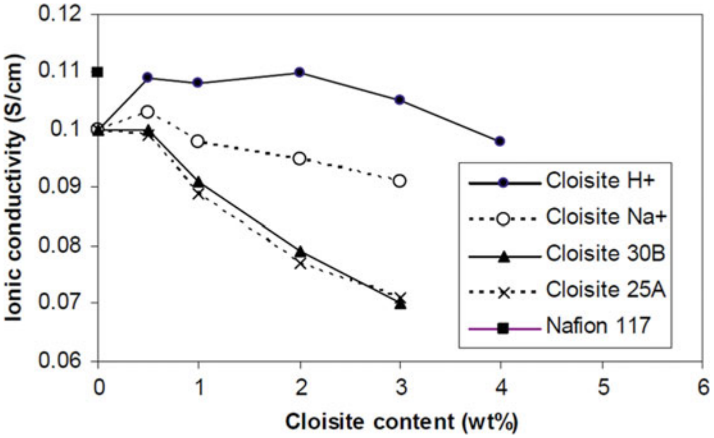


Fig. 6.9 Proton conductivities of Nafion-clay nanocomposites (Ref. [04Tho])

3 wt% of clay compared to 0.14 S cm^{-1} for the virgin Nafion at 110 °C and 100 % RH [12Mis]. Moreover, nanoclays modified with sulfonic acid containing modifier increase the proton conductivity of the resulting nanocomposite membranes due to the conducting nature of –SO_3H groups [06Béb, 10Buq]. Surface modifiers to the clay are indirectly related to the degree of dispersion of clay in the polymer matrix and play a vital role in increasing or decreasing the proton conductivity. Hence, despite the presence of the proton-conducting groups like –SO_3H, SPEEK-clay nanocomposite based on sulfanilic acid-modified clay is lower than the virgin SPEEK, while the composite based on DMDOC-modified clay is higher than the virgin SPEEK (Fig. 6.10) [11Doğ]. It is also not mandatory that the composite possessing higher water uptake will lead to enhanced proton conductivity than that of the composite having low water uptake. However, highly exfoliated morphologies of the nanofillers do play a role in enhancing the proton conductivity of the membranes (Fig. 6.11) [08Cho]. Inferior clay dispersions in the polymer matrix decrease the proton conductivity of the nanocomposites even upon sulfonation of the clay surface [05Rhe]. Increase in clay content in the polymer matrix also increases the proton conductivity of the nanocomposites up to certain extent, and further increase in the amount of clay is detrimental to the conductivity of the nanocomposite. This is due to the increased amount of clay aggregation in the polymer matrix [04Son, 05Kar, 06Son, 10Has]. The reduced proton conductivity in the nanocomposite membranes is mainly due to the resistance offered by the nonconducting or aggregated nanoclays toward proton migration. The types of modifier used for the nanoclay modification can contribute to a very small extent in this regard [05Gao, 07Dey, 08Has, 10Has, 10Swa].

Carbon-based nanofillers (CNT and graphene) possess high electrical conductivity, and the resulting nanocomposite membranes may cause short circuit in the fuel cell. Hence, the aspect ratio and amounts of nanomaterials need to be controlled in the membrane. Oxidation of these materials can further reduce their electrical

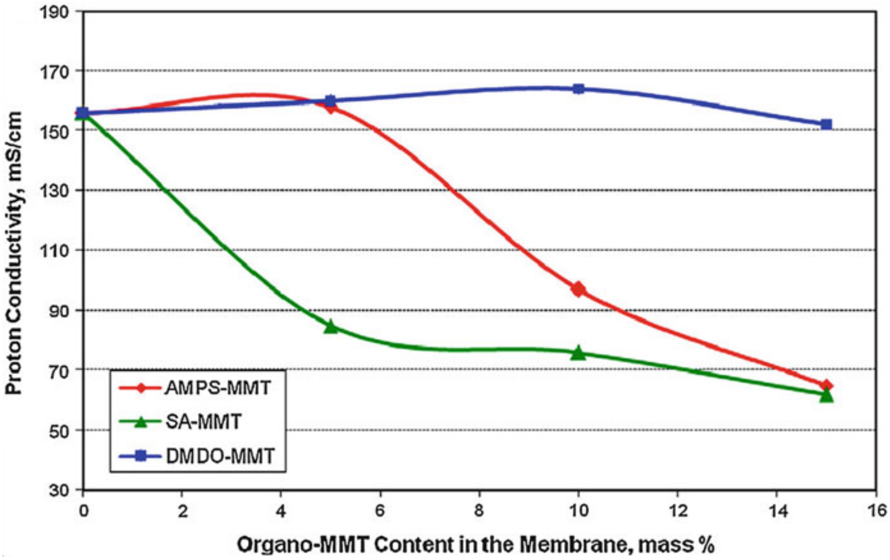


Fig. 6.10 Proton conductivities of SPEEK-clay nanocomposites with varying modifier to the clay and clay contents (Ref. [11Doğ])

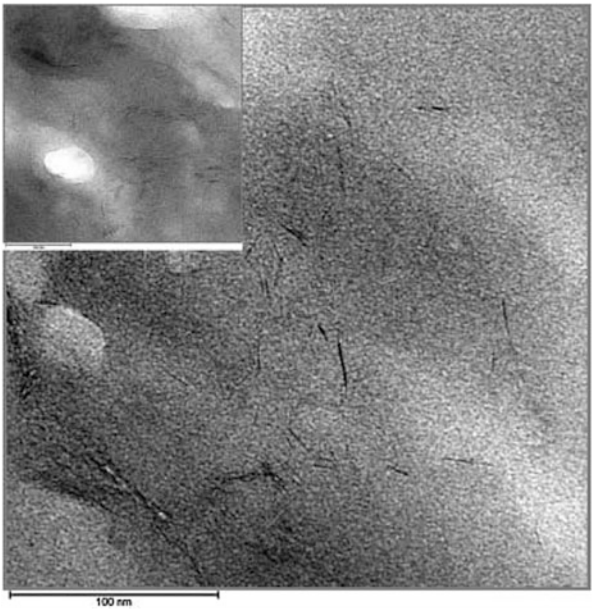


Fig. 6.11 TEM photomicrograph of SPAS-clay nanocomposites (Ref. [08Cho])

conductivities. Hence, O-CNT and GO are being used for fuel cell membrane applications. The electrical conductivities of the Nafion-MWCNT nanocomposite membranes have been found to be lower than 10^{-3}S cm^{-1} up to 5 wt% MWCNT contents [07Tho, 10Ije]. Hence, the resulting membranes are risk-free for fuel cell applications. The presence of the –COOH groups on the surface of the O-CNT increases the proton conductivity of the nanocomposites comprised of O-CNT compared to that of the MWCNT [07Tho]. Addition of the sulfonated CNTs further improves the proton conductivity of the composite membranes, and it has reached a proton conductivity value of 0.0155 S cm^{-1} for the composite compared to 0.0101 S cm^{-1} for pure Nafion [08Kan].

The transportation of proton in phosphoric acid-doped PBI membranes is mainly by the rapid proton exchange via hydrogen bonds between phosphate ($-PO_4^{2-}$) and N-heterocycles of PBI and through the self-diffusion of phosphate ions. The transference numbers for $H_2PO_4^-$ anion and for proton are 0.02 and 0.98, respectively, due to the smaller size of protons. Hence, increasing the local density of proton-conducting groups such as phosphonate groups (present on the functionalized CNTs) is beneficial for proton conduction via hopping mechanism rather than via vehicle mechanism. Thus, the proton conductivity of the acid-doped PBI-functionalized CNT-based composite membranes is almost half an order higher than the acid-doped PBI membrane without CNT [10Kan].

The presence of –OH and –COOH groups on the surface of GO results in the transportation of proton via hopping mechanism, thereby enhancing the proton conductivity of the Nafion membrane from 0.092 to 0.170 S cm^{-1} for merely 4 wt% GO content in Nafion at 80 °C and 100 % RH. This is further evident from the decreased activation energy of the composites from 14.20 to 12.98 KJ mol^{-1} [12Kum]. Addition of functionalized GO further improves the proton conductivity of the nanocomposites [11Zar]. In contrast, the barrier effect of the GO toward proton migration has also been reported to decrease the proton conductivity of the Nafion-GO composites [12Cho].

Cell Performance

The suitability of a particular membrane for fuel cell application can be determined by its cell performance study. By this study, the current densities and power densities can be determined at a particular voltage, temperature, and humidity.

The current densities of the membranes are highly dependent on the temperature, humidity, operating voltage, and membrane thickness. The commercial Nafion membranes NRE 212 (with a thickness of 50.8 μm) and NRE 211 (with a thickness of 25.4 μm) show maximum power densities of 0.97 and 1.27 W cm^{-2}, respectively, at 80 °C and 100 % RH [11Fat]. Addition of the sulfonated clay paves the path for easier proton migration in the Nafion membrane as evidenced by the enhanced power density of the nanocomposites. The maximum power densities of Nafion-clay nanocomposites comprised of sulfonated Laponite are noted to be 1.36 and 1.41 W cm^{-2}, respectively. In addition, the sulfonated clay also enhanced the current density of Nafion from 600 to 720 mA cm^{-2} at 0.6 V, 80 °C, and 100 % RH. The effect of the clay content in the polymer matrix toward the cell performance is similar to those of other physical properties described earlier, and the current densities and power densities of the nanocomposites increase up to certain amount of clay and then deteriorates with further increase in the clay content due to increased

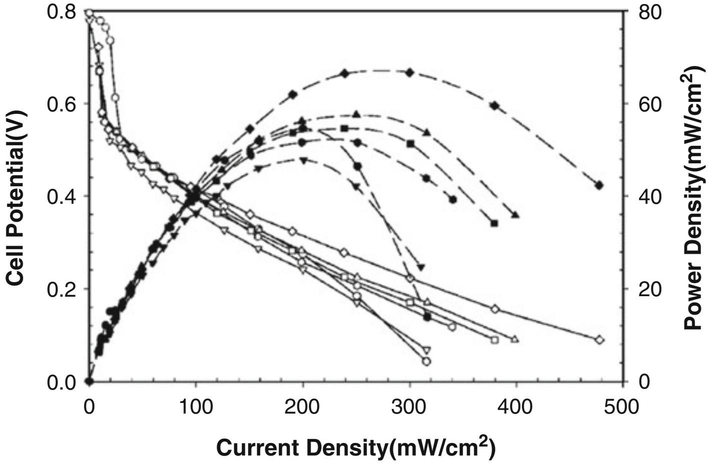


Fig. 6.12 Polarization curves of Nafion115 and Nafion-clay nanocomposites operated at 40 °C (2 M methanol/air flow rate): ● Nafion 115, ▼ Nafion-3 wt% unmodified MMT, ■ Nafion-3 wt% sulfonated MMT, ♦ Nafion-5 wt% sulfonated MMT, ▲ Nafion-10 wt% HSO_3-MMT, ⬢ Nafion-15 wt% sulfonated MMT. The same symbols (but open ones) denote cell potentials for corresponding samples (Ref. [05Rhe])

aggregation of clay beyond certain extent (Fig. 6.12) [05Rhe]. The effects of the counterion to the clay on the fuel cell performance have been investigated by Thomassin et al. The highest and lowest fuel cell performances of the Nafion-clay nanocomposites are observed for the nanocomposites comprised of Cloisite H^+ (with H^+ counterion) and Cloisite 30B (with alkyl ammonium counterion), and the performance of Cloisite Na^+ (with Na^+ counterion)-based nanocomposite remained in between. The current densities of Nafion 117 and Nafion-Cloisite H^+ are found to be 100 and 60 mA cm^{-2}, respectively, at 80 °C and 0.3 V [04Tho].

Addition of functionalized CNT to PBI membrane has resulted in an enhancement in power density by 40 % compared to the pure PBI membrane. Similarly, the current densities of the pure PBI and functionalized CNT-based composite membranes are 625 and 400 mA cm^{-2}, respectively, at 0.6 V due to the lower activation loss in the case of composite membranes (Fig. 6.13) [10Kan]. In a similar study, the maximum power density and peak power density of the Nafion-GO composites have been found to be 415 and 212 mW cm^{-2} compared to 272 and 56 mW cm^{-2} for virgin Nafion. Similarly, the current density of the nanocomposite at a cell voltage of 0.47 V has been noted to be 0.44 A cm^{-2}, which is ∽3.2 times higher than Nafion 212 (0.166 A cm^{-2}) [12Kum]. Addition of GO to Nafion has not only enhanced the proton conductivity but also the fuel cell performance as shown in Fig. 6.14 [11Zar]. Choi et al. have reported an increase in the power density of the nanocomposites compared to pure Nafion despite lower proton conductivity of the Nafion-GO nanocomposite membranes than Nafion [12Cho].

In most of the cases, the nanocomposite membranes perform better than their virgin membranes, especially at high temperatures. The fuel cell performances of the

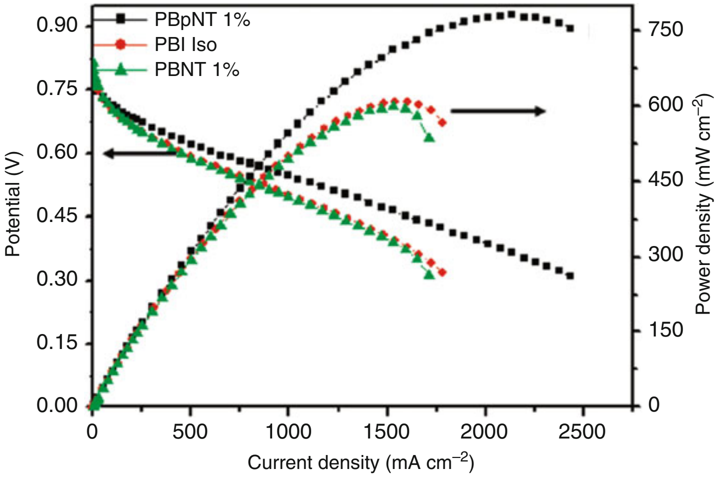


Fig. 6.13 Polarization curves for PBI-CNT nanocomposites (Ref. [10Kan])

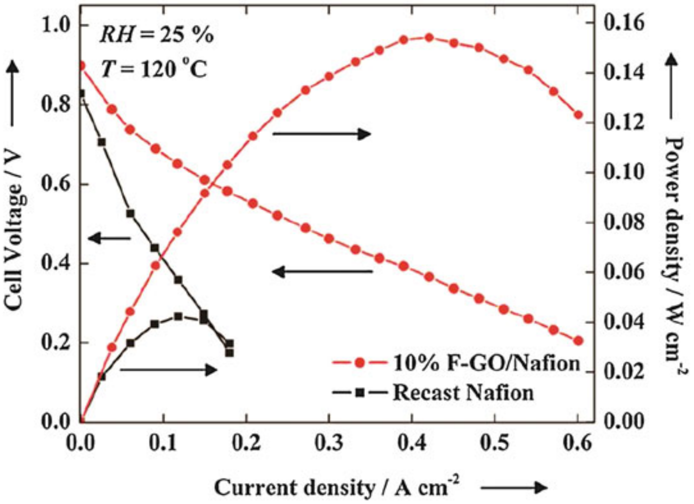


Fig. 6.14 Polarization and power density curves for recast Nafion and Nafion-GO composites with commercial E-TEK 20 wt% Pt/C catalyst (anode 0.1 mgPt cm^{-2}, cathode 0.2 mgPt cm^{-2}) in a single cell H_2/O_2 system at the temperature (T) of 120 °C and 25 % relative humidity (RH) (Ref. [11Zar])

nanocomposites are higher than their respective virgin membranes despite of their lower proton conductivity and water uptake than that of the virgin membranes. Hence, low proton conductivity and water uptake of the nanocomposites do not confer similar trend in the fuel cell performance as well. However, in all the cases, the aggregated morphology of clay in the polymer matrix leads to decreased water uptake, proton conductivity, and fuel cell performances of the nanocomposites [05Rhe, 10Kim].

6.1.2 Lithium-Ion Batteries

Owing to the decreasing fossil fuel level, volatility in oil prices in recent years and more importantly the climatic change crisis, electric vehicles with good performance, and low cost can be a necessity for gasolineless and zero emission vehicles. It is not always feasible to access the source of power generation attached to the required electronic gadget. Hence, it is necessary to store charges and deliver whenever required, and these properties are well satisfied by the availability of lithium-ion (Li-ion) battery. Li-ion batteries are the main source of power supply for electronic rechargeable devices in the present scenario. They are also used for the power supply in hybrid electronic devices and electrical vehicles [09Koj, 10Kam] and find wide applications in other industries as well [04Git]. Li-ion batteries, as the most promising candidate, must meet five criteria in order for them to enable the success of electrified vehicles: energy, power, lifetime, safety, and cost [01Nis]. Therefore, a worldwide research has been conduced to develop new generations of these batteries to fulfill the requirements. The great majority of today's lithium-ion batteries typically utilize a lithium metal oxide ($LiMO_2$, M = Co, Mn, or Ni) as cathode and crystalline graphite as anode with capacities of 160 $mAh.g^{-1}$ and 340 $mAh.g^{-1}$, respectively, and $LiPF_6$ as a salt for electrolytes. This electrochemical couple based on intercalation process (Fig. 6.15) provides a cell voltage of approximately 4 V and energy densities in excess of about 220 $Wh.kg^{-1}$. Although commercially this has proven to be highly successful cell chemistry, graphite and $LiCoO_2$ both have high coulombic efficiencies (more than 95 %) with low capacities [09Oza]. Hence, there exists a general requirement for the development of new positive and negative electrode materials to facilitate the next generation of these energy storage devices with higher capacity.

6.1.2.1 Charging-Discharging Process

The reduction and oxidation occur at the cathode and anode, respectively, in a general electrochemical cell. The anode is the negative electrode from which electrons flows out toward the external part of the circuit, while the cathode is connected to the positive pole to allow the circuit to be completed. When the cell is connected to an external load, electrons flow from the anode to the cathode through the external load. The electric circuit is completed in the electrolyte by the flow of anions and cations to the anode and cathode, respectively, and the process is called discharging. During the charging of a rechargeable battery, the current flow is reversed and the oxidation occurs at the cathode and reduction at the anode [02Lin]. In a Li-ion battery, Li-ion moves from the anode to the cathode while discharging and back when charging. The amount of Li-ion that can be stored reversibly in the two electrodes is represented as the storage capacity of the battery. The Li-ions are extracted from the $Li_{1-y}MO_2$ electrode during the charging process and

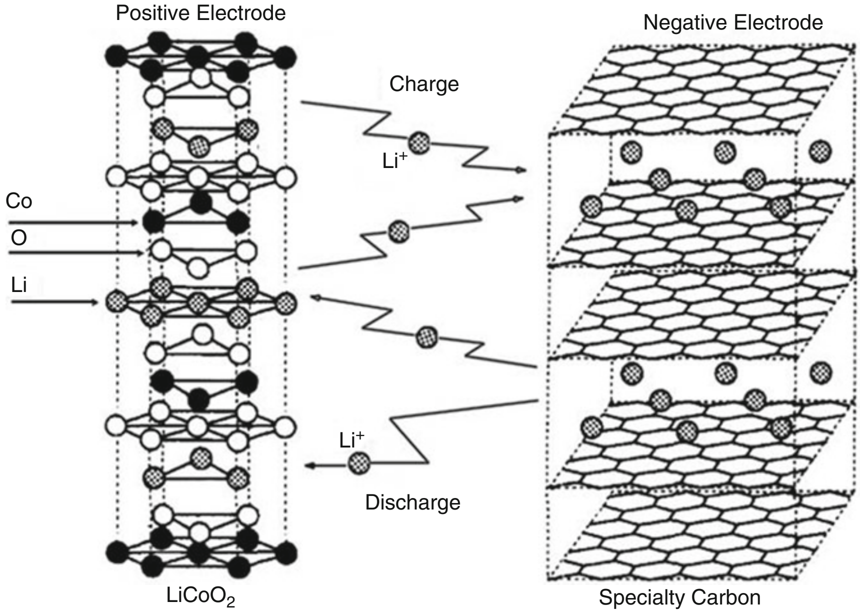


Fig. 6.15 Schematic diagram of the chemical reaction of the lithium-ion battery (Ref. [10Kam])

simultaneously inserted into the graphitic carbon electrode, coupling with the negatively charged electrons to maintain overall charge neutrality. Li-ions are reversibly extracted from the negative electrode and inserted into the positive electrode during the discharging process. The anodes and the cathodes are separated by a porous polymer membrane.

6.1.2.2 Carbon-Based Anode

Figure 6.16 shows that highly conducting carbon nanostructures offer very interesting reversible capacity compared to others and can be considered as future anode materials. The carbon materials can be classified mainly into soft carbon, i.e., graphite, and hard carbon, i.e., disordered carbon and nanostructured carbon [09Naz]. The capacity of Li-ion batteries based on graphite as an anode material can be theoretically limited due to the combination of Li-ions with every second carbon hexagon in graphite sheets [13Xio]. On the other hand, its allotrope CNTs has shown much improved Li capacity compared to graphite, due to their unique structures and properties. CNTs have been reported to display conductivities as high as 106 $S \cdot m^{-1}$ and 105 $S \cdot m^{-1}$ for single and multi-walled carbon nanotubes, respectively [99And]. Recently, research is mainly focused on CNT-based anodes for lithium-ion batteries.

Theoretically, using a Li metal anode is the best way of delivering high energy density due to its very large theoretical capacity of more than 3800 $mAh.g^{-1}$ compared to 372 $mAh.g^{-1}$ for LiC_6. However, a pure lithium metal as negative

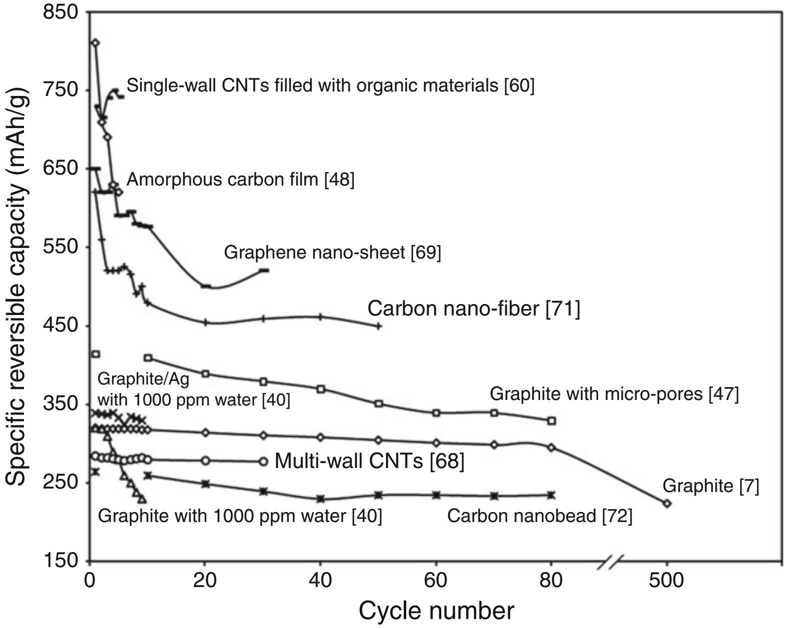


Fig. 6.16 Specific reversible capacity versus cycle number for different kinds of carbonaceous materials (Ref. [10Kam])

electrode is difficult to cycle and possesses a short cycle life. Moreover, it is also extremely dangerous due to the change in shape of the electrode upon charging-discharging process, dendrite formation, and reactions with the electrolyte. Meanwhile, high reactivity of Li and its low melting point (180 °C) may lead to firing and explosion for minor reasons (such as an internal short circuit which increases the temperature of the cell above 180 °C) [08Gup]. Li anodes are also being improved by coating its surface using fullerene to enhance the electrochemical performance [09Ari] or using a special cross-linked gel electrolyte to inhibit dendrite formation up to a certain extent [01Tat]. Several other possible alternatives for graphite anodes consist of group IV (Si, Ge, Al, Sn) and group V (Sb, Bi, In) elements [99Win, 03Lin, 07Bry, 08Che, 09Arr, 09Cui, 09Yoo]. This is due to their ability to react reversibly with large amounts of Li per formula unit to form Li metal intermetallics according to following reversible reaction

$$\mathrm{xLi^+ + Me^+xe^- \leftrightarrow Li_xMe} \tag{6.5}$$

where Me is a lithium reactive metal.

6.1.2.3 Carbon Nanotubes and Nanofibers

Carbon nanotubes and nanofibers are potential candidates for Li-ion battery due to their highly conducting nature and high aspect ratio.

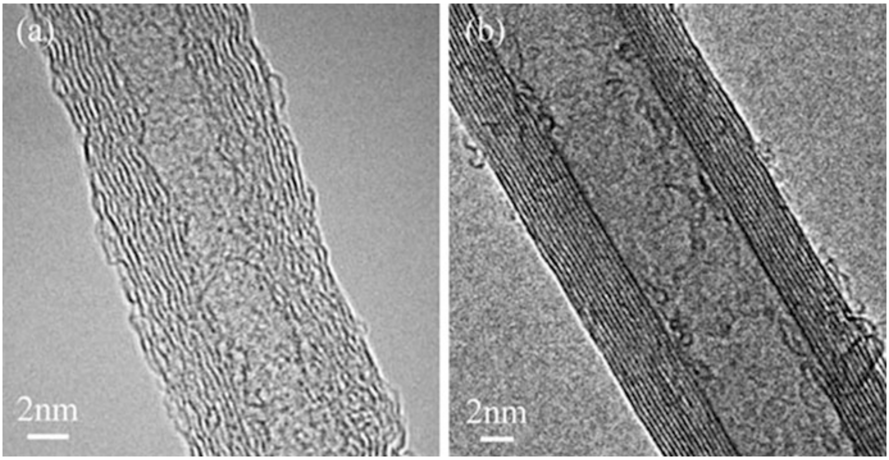


Fig. 6.17 High-resolution TEM images of CNTs with (**a**) defect-rich surface and walls and (**b**) well-ordered graphitic walls (Ref. [10 Su])

As Active Materials for Electrodes

CNTs are used in various areas due to their outstanding electrical properties, strong mechanical strength, high chemical stability, high aspect ratios, and high activated surface areas. Applications of CNTs as electrodes in Li-ion batteries [97Wit, 00Cla] enhance the Li storage capacities to an extent higher than that of LiC_6 composition of graphite. Li-ions can be stored in electrodes comprising of CNTs via the following three ways: (1) intercalation, (2) adsorption and accumulation on the surface, and (3) storage in the void space between bundles of tubes. Texture is an essential aspect of CNTs with regard to their application in Li-ion batteries. Commercially available CNTs have defects both on the surface and in the bulk [79Tes]. Su et al. [10Su] have compared the microstructure of both defected CNTs and well-ordered graphitic wall CNTs (Fig. 6.17). A complex and open interface of defective CNTs may facilitate the initial insertion of Li; however, the removal of Li is highly retarded during discharge and results in an overvoltage higher than 3 V (Fig. 6.18a) [99Fra]. This is the direct evidence that some Li-ions are not intercalated between the graphitic layers in CNTs, because intercalation and deintercalation proceed with a low-voltage profile. The very popular reagent nitric acid is a strong etchant for CNT surfaces and leaves a high concentration of reactive acidic functions on the surface [04Lak], thereby increasing the specific surface area of commercial carbon materials and changing the electrochemical performance [08Che].

Graphitization at high temperature appears to be the only way to remove defects and oxygen species from CNTs. This decreases the specific charge capacity, but increases the coulombic efficiency and cycle stability. After 20 charge-discharge cycles, the charge capacity of the less-graphitized CNTs fades to 65.3 % of their original charge capacity, but the well-graphitized CNTs maintain 91.5 % of their original charge capacity as a result of their stable structure (Fig. 6.18b)

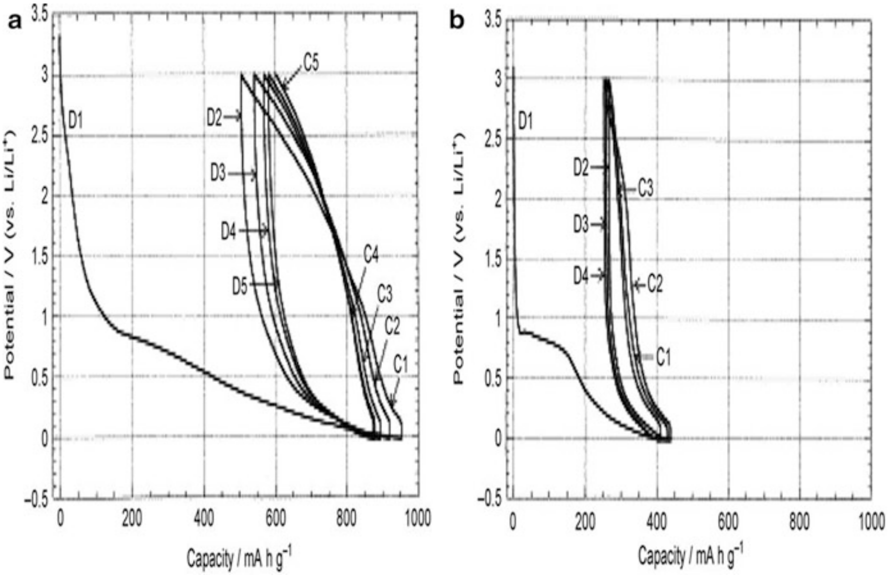


Fig. 6.18 Charge-discharge characteristics of Li insertion into (**a**) multi-walled CNTs treated at 900 °C and (**b**) multi-walled CNT heat-treated at 2000 °C at a current of 17 mAg^{-1} (Ref. [10 Su])

[00End]. Carbon nanofibers (CNFs) also exhibit a performance as electrode materials similar to CNTs depending on their morphology [04Yoo]. Although the product costs for CNF have decreased, electrodes consisting of CNFs are still not competitive, neither in prices nor performance, with those consisting of graphite. The only commercialized application of CNFs in Li-ion batteries at present is the use as filler or as additive, where the problem of stability is solved through their incorporation in a matrix [99End, 01End].

CNFs prepared by electrospinning process have also been explored as Li-ion storage materials [06Kim]. The electrospun nanofibers exhibited thin web morphologies. Porous CNFs could be collected in the form of porous mats and used directly as anodes in a Li-ion battery without adding any polymer binder or other additives.

As Additives in Electrodes

CNTs can form a network by entanglement due to their 1D structure and large aspect ratio. CNTs are used as fillers or additives for electrode materials due to their excellent electric and thermal conducting properties [06Kan, 06She]. This is currently the only commercialized use of CNTs in Li-ion batteries [06Pan]. Figure 6.19 shows the texture of a composite anode, which exemplifies the value of CNTs but clearly shows a long way that has to be travelled prior to achieve a suitable and stable electrode. Su et al. [10Su] has speculated that a complete bottom-up approach (in which synthesis of a hierarchically structured carbon with the combination of CNTs and a reactive organic matrix to form the final electrode) is the most appropriate procedure.

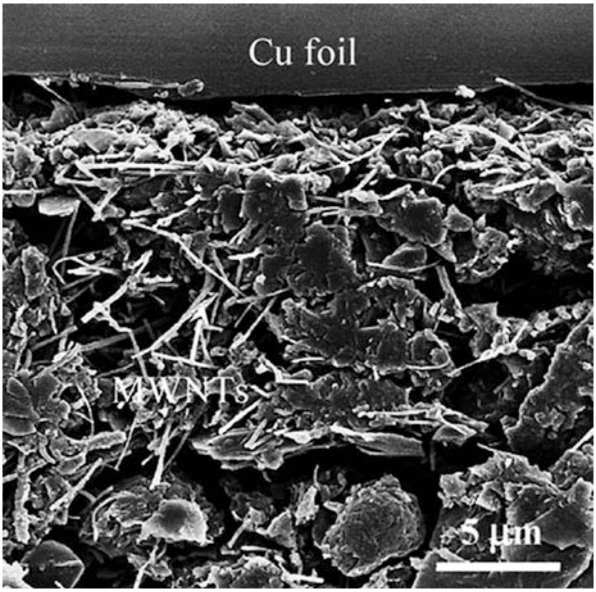


Fig. 6.19 SEM image of a carbon anode in a commercial cell in which multi-walled CNTs were used as additive (Ref. [10 Su])

6.1.3 Supercapacitors

Supercapacitors, also called electrochemical capacitors (ECs) and ultracapacitors [06Pan], are supposed to be an alternative energy storage device due to their high-rate capability, pulse power supply, long cycle life, simple principles, high dynamics of charge propagation, and low maintenance cost [08Mil, 08Sim]. Conventional capacitors possess high power densities, but the energy density is very low compared to fuel cells and batteries (Fig. 6.20) [00Kot]. Hence, batteries can store more charges compared to capacitors, but cannot deliver quickly due to low power density. However, capacitor can store less charge but can deliver quickly producing huge amount of power. Supercapacitors consist of two electrodes separated by a dielectric material and immersed in the electrolyte solution. Supercapacitors store charges using two types of capacitive behaviors: (1) electrical double-layer capacitance (EDLC) generated due to the electrode potential-dependent accumulation of charge at the electrode-electrolyte interface and (2) pseudo-capacitance developed due to the fast reversible surface redox processes at characteristic potentials.

Specific capacitance of EDLC is measured using following equation:

$$C = \left(\frac{\epsilon_r \epsilon_0}{d}\right) A \tag{6.6}$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of vacuum, d is the effective thickness of the EDLC and is termed as the Debye length, and A is the specific surface area of the electrode. However, the derivative ($d\Delta q/d\Delta q$) provides the pseudo-capacitance where Δq is the change in charge acceptance and Δv is the change in voltage.

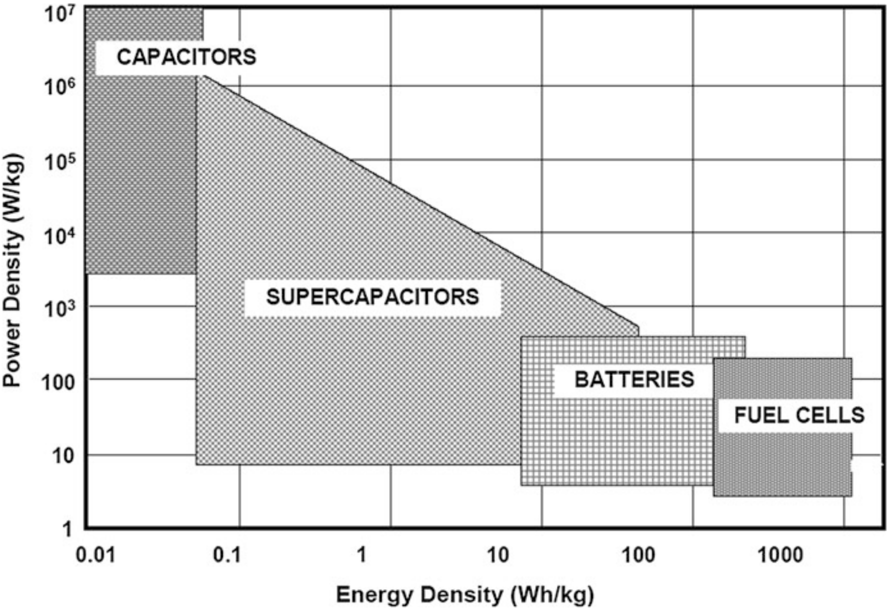


Fig. 6.20 Ragone plot of energy conversion and storage (Ref. [00Kot])

The energy density (E) and power density (P) in a supercapacitor can be calculated using following equations:

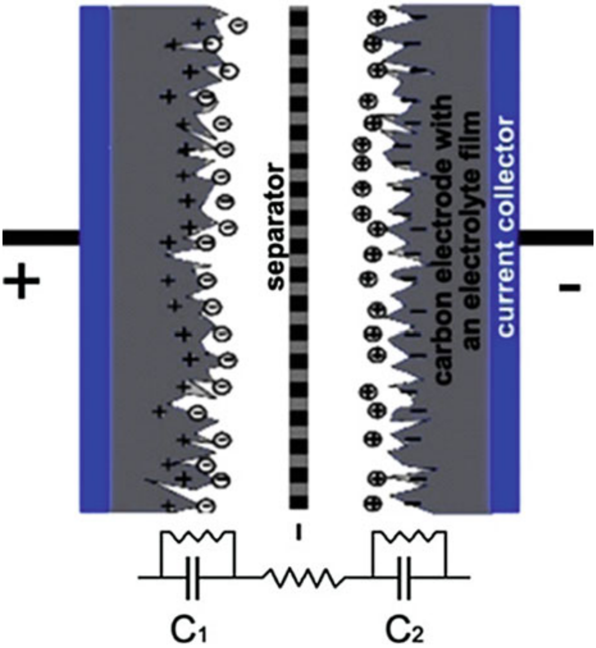
$$E = \tfrac{1}{2}CV^2 \tag{6.7}$$

$$P = V^2/4R_s \tag{6.8}$$

where C is the total specific capacitance of the cell (EDLC + pseudo-capacitance), V is the applied cell voltage, and R_s is the equivalent series resistance. This indicates that the essential requirements for the fabrication of a supercapacitor with high performance are large specific capacitance, high cell voltage, and minimum equivalent series resistance value. The selection of electrolyte solution and electrode material is the most decisive factor to optimize the overall performance of the supercapacitor.

The basic operating principles of conventional capacitors and supercapacitors are similar but with minute changes in the types of electrodes and dielectric materials. They can store significantly higher amounts of energy density than the conventional dielectric capacitors. The main advantage of supercapacitors is that the shortage of other power sources, such as batteries and fuel cells, could be complemented, because of their long cycle life and rapid charging and discharging rate at high power densities [00Bur]. These devices utilize high surface area electrode materials and thin electrolytic dielectrics to achieve specific capacitance of several orders of magnitude higher than the conventional capacitors. The capacitance in these devices

Fig. 6.21 Electrochemical double-layer capacitor with simplified electric circuit (Ref. [02Ste])



is stored as a buildup of charge in the layers of the electrical double layer formed at the interface between a high surface area electrode and an electrolyte [11Sno]. Generally, porous carbon materials such as activated carbon [01Fra], CNTs [00Fra, 05Du], high surface area carbon [00Yoo], and graphene [06Chm] have been used as electrodes in supercapacitors.

6.1.3.1 Highly Porous Carbon for Supercapacitors

The mechanism of the charge storage in EDLCs as illustrated in Fig. 6.21 is based on the activated carbons with capacitance proportional to the electrode surface area [02Ste]. The supercapacitors are operated by adsorbing/desorbing charged ions from electrolyte onto their porous high surface area electrode. The charging is also achieved by the dissociation of ions in the electrolyte salts, resulting in charge separation distance in the order of 1 nm. This arrangement occurs inside the pores of high surface area carbon materials.

6.1.3.2 High Surface Area Carbon for Supercapacitors

Currently, supercapacitors are produced by pyrolyzing and activating wood, plant matter, petroleum sources, and phenolic resins (including aerogels and cryogels) [07Bur, 08Obr]. Naturally derived electrodes contain great amounts of impurities or ash, which can compromise the supercapacitors' performance [99Con] due to unwanted faradaic reactions that can degrade the electrolyte. Carbon nanotubes and graphenes have also been used in the manufacturing of batteries and supercapacitors because of their high conductivity [06Fen].

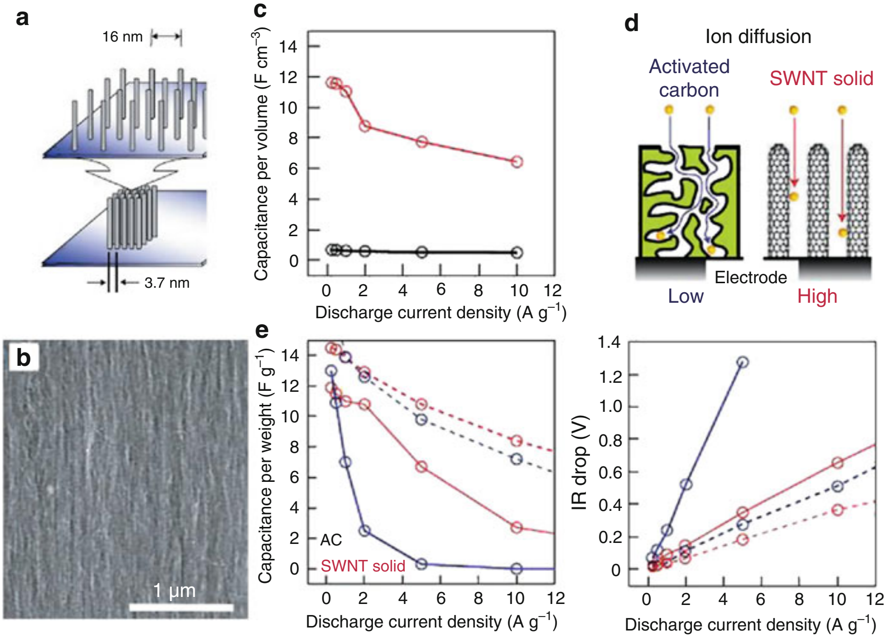


Fig. 6.22 Comparison of activated carbon and oriented CNT. (**a**) Fluid drying to form dense solid carbon from long SWCNTs, (**b**) TEM image of the nanotube solid, (**c**) capacitance per volume for dried (*red*) and as prepared (*black*) SWCNTs, (**d**) ion diffusion in activated carbon and oriented CNTs, (**e**) specific capacitance as a function of current density (results from CNTs are in red, and activated carbon is in *blue*), and (**f**) potential drop as a function of current density (Ref. [02Ste])

CNTs for Supercapacitors

CNTs with large surface areas have been extensively studied in supercapacitors [06Kim] and may have advantages over traditional carbon as shown in Fig. 6.22 [05Gut]. A maximum specific capacitance of 180 F.g^{-1} with a large power density of 20 kW.kg^{-1} has been achieved by heating CNTs to enhance their specific surface area and pore distribution [01An]. The surfaces of CNTs have also been treated with ammonia, aqueous NaOH/KOH solution, or nitric acid to introduce oxygen functional groups (carboxyl, phenolic, lactone, aldehyde, ether groups, etc.), thereby improving the electrochemical properties of the electrodes [01Fra]. Surface treatments of the CNT electrode using ammonia plasma have been found to increase the capacitance from 38.7 to 207.3 F.g^{-1} [04Yoo]. However, the presence of the oxygen groups in CNTs is considered to escort the capacitor toward instability with an increased resistance and deterioration of capacitance [06Pan]. In addition, the introduction of surface oxygen groups to the CNT electrodes will not work with organic electrolyte.

Graphene-Based Asymmetric Supercapacitors

Graphene has been considered to be a potential candidate for its application as supercapacitor electrode. In order to improve the capacitance of carbon-based supercapacitors metal oxide such as RuO_2, IrO_2, MnO_2, and NiOx are used, as they can contribute toward the pseudo-capacitance apart from the double-layer capacitance from carbon materials [07Lee]. On the other hand disadvantage of using metal oxides is their low abundance and high cost [07Zhe].

Development of high-voltage asymmetric supercapacitor with graphene as negative electrode and MnO_2-graphene composite as the positive electrode in aqueous Na_2SO_4 solution electrolyte has been carried out by Wu et al. [10Wu]. The superior electrical conductivity of graphene makes a nanostructured MnO_2-graphene composite, which is promising for use as faradic electrodes in asymmetric supercapacitors. In another work, Bao, Cui, and coworkers [11Yu] have demonstrated a novel structure of a supercapacitor electrode based on graphene-MnO_2 textiles (Fig. 6.23). The hybrid graphene-MnO_2-based textile could yield specific capacitance values up to 315 $F.g^{-1}$ at a scan rate of 2 $mV.s^{-1}$. Graphene sheets with either individual single-layered sheets or few-layered graphite can offer an ideal

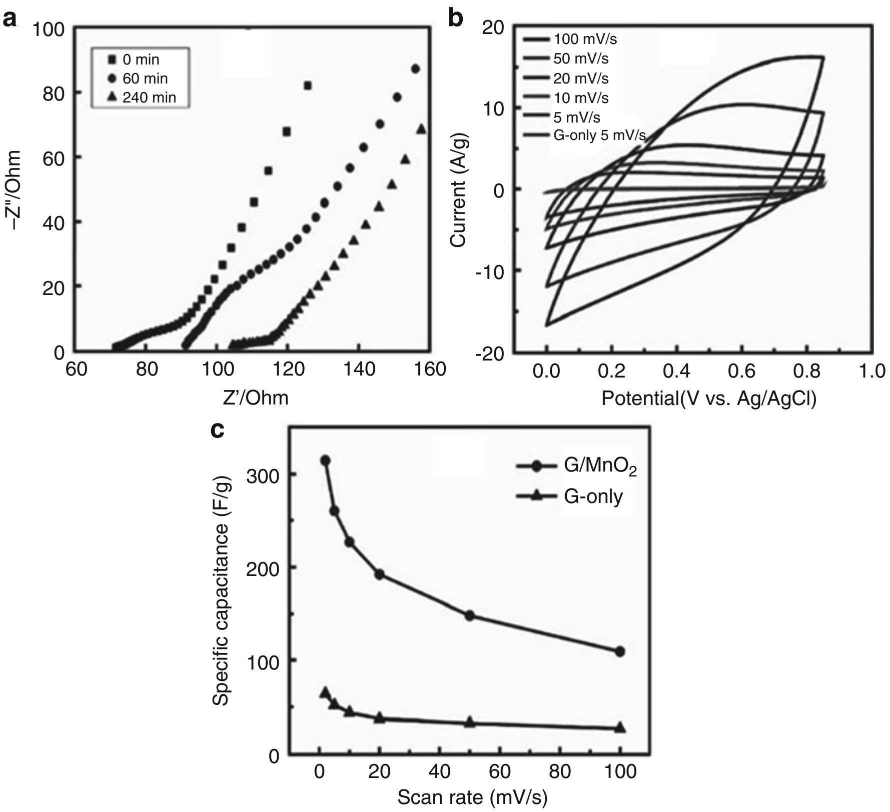


Fig. 6.23 Supercapacitors based on graphene-MnO_2 textiles. (**a**) Impedance of graphene-MnO_2 textiles with different MnO_2 deposition time, (**b**) cyclic voltammograms for graphene-MnO_2-textile electrode at different scan rates, and (**c**) comparison of specific capacitance values between graphene-MnO_2 textile and a graphene-nanosheet-only textile at different scan rates (Ref. [12Yi])

structure for ion absorption of MnO_2. A novel kind of asymmetric supercapacitor using agraphene-MnO_2 composite as the positive electrode and activated carbon nanofibers (ACN) as the negative electrode in a neutral aqueous Na_2SO_4 electrolyte have also been developed by Fan et al. [11Fan]. Wang et al. [11Wan] has grown $Ni(OH)_2$ nanoplates and RuO_2 nanoparticles on high-quality graphene sheets to maximize the specific capacitances of these materials. Subsequently, $Ni(OH)_2$-graphene electrode and RuO_2-graphene electrode have been paired up to afford a high-performance asymmetrical supercapacitor with high energy and power densities, operating in aqueous solutions at a voltage of 1.5 V.

These high performances were considered to be mainly attributed to the advanced hybrid electrode materials and their unique pairing.

6.1.4 Graphene-Based Polymer Composite

Several polymers including conducting polymers have been used to enhance the specific capacitance values of the supercapacitors. These include polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), and sulfonated polyether ether ketone (SPEEK). The role of these polymers is to enhance the pseudo-capacitance value of the supercapacitors by the redox reactions occurring while charging and discharging process. The graphene-PANI composite has shown a specific capacitance of 300–500 $F.g^{-1}$ at a current density of 0.1 $A.g^{-1}$ with a very good cycling stability [11Góm]. Substantially high capacitance value (978 $F.g^{-1}$) of the graphene nanosheet (GNS)-PANI composite prepared via in situ polymerization technique has been noted due to the homogeneous dispersion of PANI over the GNSs with large surface area [10Yan]. Nanostructured PPy and highly electrically conductive graphene nanosheets have also been employed in a multilayered configuration to attain high SC and low electronic resistance for supercapacitor electrode applications [10Bis]. Graphene-PEDOT composite electrodes suitable for supercapacitor applications have shown specific capacitance of 1410 $F.g^{-1}$ and at a scan rate of 40 $mV.s^{-1}$ [14Jac]. Water dispersible graphene functionalized with SPEEK shows a specific capacitance of 476 $F.g^{-1}$ at a current density of 6.6 $A.g^{-1}$ [12Kui].

6.2 Summary and Future Prospects

The rapid depletion of fossil fuels and increased pollution has rendered to the development of energy conversion and storage devices. Fuel cells, Li-ion battery, and supercapacitors are the potential candidates for these purposes.

In the case of a fuel cell membrane, the addition of nanomaterials to polymer membranes enhances the physical properties including the proton conductivity and performance of the membranes provided the nanomaterial does not act as a barrier toward proton migration from anode to the cathode. This can be achieved using suitable modifier and improving the degree of dispersion. Despite plenty of work that has already been performed in this direction, till now no breakthrough has been achieved, and a lot more need to be done prior to the end application.

Lithium content of intercalated compound of carbonaceous materials can be increased from LiC_6 for graphite to higher amounts such as $Li2.7C_6$ for CNTs and $Li2.9C_6$ for carbon nanoparticles, which offer much more capacity. Recently, CNTs are used to replace graphite-based anodes. CNT-based anodes together with small improvements in Li storage capacity and cyclability compared to graphite-based anodes make it difficult to use them for replacing graphite-based anodes in Li-ion anode. It seems that the most promising attempts at improving Li-ion anodes may come from the combination of CNTs with other lithium storage compounds with complex nanostructure designs. Polymer-based nanocomposites as electrolyte and electrode material have also been investigated. Further studies are required to improve its long-term stability.

Mainly, carbon-based materials are being used as supercapacitors electrode. Graphene-based materials are indeed very fascinating materials with great potential in the active field of supercapacitors. It is providing high specific capacitance in combination with polymeric materials. In theory, graphene has been considered to be the ideal supercapacitor electrode material due to its extremely large surface area, extraordinarily high electrical conductivity, and strong mechanical strength. In practice however, massive efforts are still needed to turn this promising material into a real practical material.

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Polymer Nanocomposites for Automobile Engineering Applications

7

Arup Kumar Chandra and Nalini Ranjan Kumar

7.1 Introduction

Individual mobility is a basic need of people and an important prerequisite for the development of modern societies. In this regard, the automobile plays a crucial role. The United Nations estimates that the worldwide vehicle fleet will be double from 850 million today to approximately 1.5 billion by 2030. This development is driven by a rising demand in rapidly growing markets especially like Brazil, Russia, India, China, and South Africa. The increasing prosperity of these regions will lead to a greater desire for more individual mobility of people, who will be buying more and more vehicles. With the traffic volume increasing, the worldwide energy demand will rise as well. Questions concerning passenger safety, intelligent traffic guidance systems, reduction in pollution, and effective recycling at the end of the value-added chain to save scarce resources are becoming more urgent. Therefore, companies and research institutes worldwide are focusing their research and development efforts more and more on adapting the safety, comfort, and eco-friendliness of the automobile to meet future needs; at that the same time the advantages of individual mobility can be ensured in a sustainable way. In this context, nanotechnology is playing an important role, if not decisive one. Nanotechnology is an exciting area of scientific development which promises "more for less." It offers ways to create smaller, cheaper, lighter, and faster devices that can do more and cleverer things, use less raw materials, and consume less energy.

Research work is being carried out in many applications of nanotechnology such as improved tires, lubricants, fuel cells for clean energy, lighter and stronger engine

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and body materials, better catalysts, nanoporous filters, self-cleaning windshields, self-healing and scratch-resistant coatings, environment-friendly corrosion protection, and color-changing paints to name but a few [03Her, 06Cha, 08Cha, 08Wer, 13Cha]. Major advances are also being made in the use of polymer nanocomposites for body panels as these can be made lightweight yet rugged, and in new metal nanocomposites to improve engine efficiency. Cars are notable for progressively increasing their high-technology content, using smart nano-sensors for the prevention of possible problems from a tire blowout to break failure, even to avoid a collision.

Vehicle manufacturers are keen to be more environmental friendly in their manufacturing processes as well as in the final product. Investigations are underway: how nanotechnology may lead to a reduction in toxic wastes and by-products by substituting hazardous reactants and solvents or, better still, by using nanomaterials/nanotechnology to eliminate their need altogether.

7.2 Nanomaterials and Nanotechnology

7.2.1 What are Nanomaterials?

Nano originates from the Greek word meaning "dwarf," i.e., very small or tiny. A nanometer is one billionth (10^{-9}) of a meter, only the length of ten hydrogen atoms, or about one hundred thousandth of the width of a hair. Nanoscale materials are defined as a set of substances having at least one dimension less than approximately 100 nm. Nanomaterials are of interest because at this scale unique mechanical, optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, automobile, and other fields.

7.2.2 What is Nanotechnology?

Scientists have manipulated matter at the nanoscale for centuries; however, progress was not substantial until a new generation microscope was invented in the 1980s in IBM, Switzerland. It was only through this microscope the world of atoms and molecules could be visualized and also realized and that they could be managed [08Wer].

Basically, nanotechnologies are interface technologies that include many different science and application areas. Among them are classical fields of knowledge such as chemistry, physics, and mechanical engineering as well as new disciplines such as nano-biotechnology and subareas of microelectronics. In that context, nanotechnologies have become increasingly important over the last few years. Today, nanoparticles with new characteristics are already being produced on a large scale and integrated into products. In most cases, the nanotechnological products currently available on the market are rather unspectacular and have become an almost unperceived part of daily life. The purpose of nanotechnologies is the production and examination of functional structures smaller than 100 nm. At this

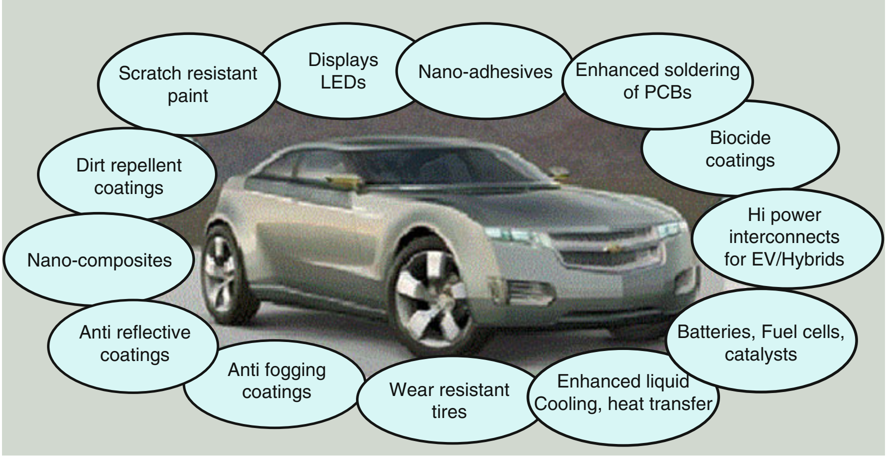


Fig. 7.1 Application of nanotechnologies in automobile engineering [10Wal]

scale, material-dependent interface effects and large specific surfaces observable become more important. At this order of magnitude, quantum effects appear that exhibit unique potential for novel functionalities. The critical size below which material properties change depends on the material itself. By changing the size of such components, the control of the chemical composition, and the targeted manipulation of the atomic structure, it is possible to produce macroscopic materials with radically new properties and functionalities.

Since nanotechnologies are solely defined by the geometric length scale and the related physical, chemical, and biological effects, almost all branches of industry are affected by it. The specific surface of a gram of nanocrystalline powder can have the size of a soccer field depending on the grain size of the material. In general, the application of nanomaterials in the automobile industry is growing as shown in Fig. 7.1.

This chapter attempts to discuss the applications of nanotechnology in automobile engineering and bring some examples of products being used in car manufacturing industries today.

7.3 Nanocomposites

Nanocomposites are materials that incorporate nanosized particles into a matrix of standard material such as polymers. Such addition of nanoparticles can generate a drastic improvement in properties that include mechanical strength, toughness, and electrical or thermal conductivity and also processing behavior. The effectiveness of the nanoparticles is such that the amount of material required to add is normally 0.5–5.0 % by weight. They have properties that are superior to conventional micro-scale composites and can be synthesized using simple and inexpensive techniques.

7.3.1 Polymeric Nanocomposites

When nanofillers, nano ingredients, nano rubber, or any other nanoscaled particles are incorporated and dispersed in polymer matrix, the resultant composite is known as polymeric nanocomposite. Polymers reinforced with as little as 2 % to 6 % of these nanoparticles via melt compounding or in situ polymerization exhibit dramatic improvements in properties such as thermomechanical, lightweight, dimensional stability, barrier properties, flame retardancy, heat resistance, and electrical conductivity.

Polymeric nanocomposites are organic–inorganic hybrid materials where the inorganic phase like nanosilica, nano-ZnO, and nanoclay is distributed in nanoscale within the organic polymer matrix. Increased surface area of nanofillers produces better interfacial polymer–nanofiller interaction. This results in enhancement of mechanical and other properties which have a wide potential in the electronic, magnetic, optical, and chemical field as well. In polymeric nanocomposites (PNCs), the polymer could be thermoplastic or thermosetting in nature.

7.3.1.1 Advantages of Nanocomposites

Improvement in mechanical properties has resulted in major interests in nanocomposite materials in numerous automotive and general/industrial applications.

The main advantages offered by nanocomposites are [95Mes, 95Oka, 99Gil, 04Ban]:

1. Lighter weight due to low filler loading
2. Improved properties compared to conventional filler-based composites at very low loading of filler
3. Optimization of conflicting properties
4. High thermal stability
5. Improved impermeability to gases, vapor, and liquid
6. Good optical clarity
7. Improved flame retardancy with reduced smoke emission
8. Tailor-made electrical conductivity
9. Better wear properties

Besides their improved properties, these nanocomposites are also easily extrudable or moldable to near final shape. Since high degrees of stiffness and strength are realized with little amount of high-density inorganic materials, they are much lighter compared to conventional polymer composites. This weight advantage could have significant impact on environmental concerns among many other potential benefits. By surveying the nanocomposites prepared so far, wear resistance polymeric nanocomposites can be regarded as a successful example that brings the so-called nanoeffect into full play. At a filler loading of less than 1 %, the wear rate of the matrix was lowered by over thousand times. Similar enhancement due to the addition of small amount of fillers is impossible to perceive in micro composites. The developments in this aspect have broadened the application possibility of particulate composites and solved the dilemma arising from the contradiction

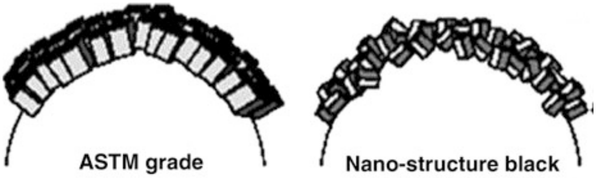


Fig. 7.2 ASTM-grade carbon black and nanostructured carbon black [06Cha]

between performance improvement and processibility deterioration, as often observed in microparticle-filled composites. The main reason for improved properties is due to smaller and highly disordered structure of nanofillers that results in more active sites with a higher surface energy and ultimately leads to stronger mechanical/physiochemical interaction with polymers (Fig. 7.2) [06Cha].

7.3.2 How Nanocomposite Works?

Nanoparticles have an extremely high surface-to-volume ratio which dramatically changes their properties when compared with their bulk-sized equivalents. It also changes the way in which the nanoparticles bond with the bulk material. The result is that the properties of composite can be improved many times with respect to the component parts.

7.3.3 Current Applications of Nanocomposites

Applications of nanocomposite are diversified such as thin film capacitors for computer chips; solid polymer electrolytes for batteries, automotive engine parts, and fuel tanks; impellers and blades; oxygen and gas barriers; food packaging; etc. with automotive and packaging accounting for a majority of the consumption [10Wal]. The automotive segment is projected to generate the fastest demand for nanocomposites if the cost/performance ratio is acceptable. A few nanocomposites have already reached the marketplace, while a few others are on the verge, and many continue to remain in the laboratories of various research institutions and R&D of companies. Nanocomposites comprising of nanoparticles such as nanoclays or nanocarbon fillers, carbon nanotubes, carbon nanofibers, and graphite platelets are expected to be a major growth segment for the plastic industry.

Some examples of the use of nanocomposites in automobiles include the following: step assist – first commercial application on the 2002 GMC Safari and Chevrolet Astro van, body side molding of the 2004 Chevrolet Impala (7 % weight savings per vehicle and improved surface quality compared with TPO and improved scuff and mar (scratch, rub, wear, etc.) resistance), cargo bed for GM's 2005 Hummer H2 (7 lbs of molded-in-color nanocomposites), fuel tanks (increased resistance to permeation), under-hood timing gauge cover (Toyota), and engine cover (Mitsubishi) [10Wal].

7.4 Nanofillers Used in Polymeric Nanocomposites

Fillers are used in polymers for a variety of reasons: cost reduction, improved processing, density control, optical effects, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy, and improved mechanical properties, such as stress–strain properties, hardness, tear resistance, etc. Each filler has different properties, and these, in turn, are influenced by the particle size, shape, particle morphology, and surface chemistry. Amorphous silica, carbon black, and clay are the most widely used particulate fillers in the polymer industry to achieve the performance requirements in various engineering applications. The degree of improvement of these performance requirements by these particulate fillers in polymer–filler composites mainly depends on the size of dispersed fillers, polymer–filler interaction, and morphology of the fillers. Nanofillers are a class of new-generation fillers, which have at least one dimension in the order of nanometer and within 100 nm (given in Fig. 7.3). This new class of material has varying shapes ranging from isotropic needlelike, particulate sphere, or sheetlike elements. Uniform dispersion of these nanosized particles can lead to ultra-large interfacial area between a polymer and the fillers. This large interfacial area

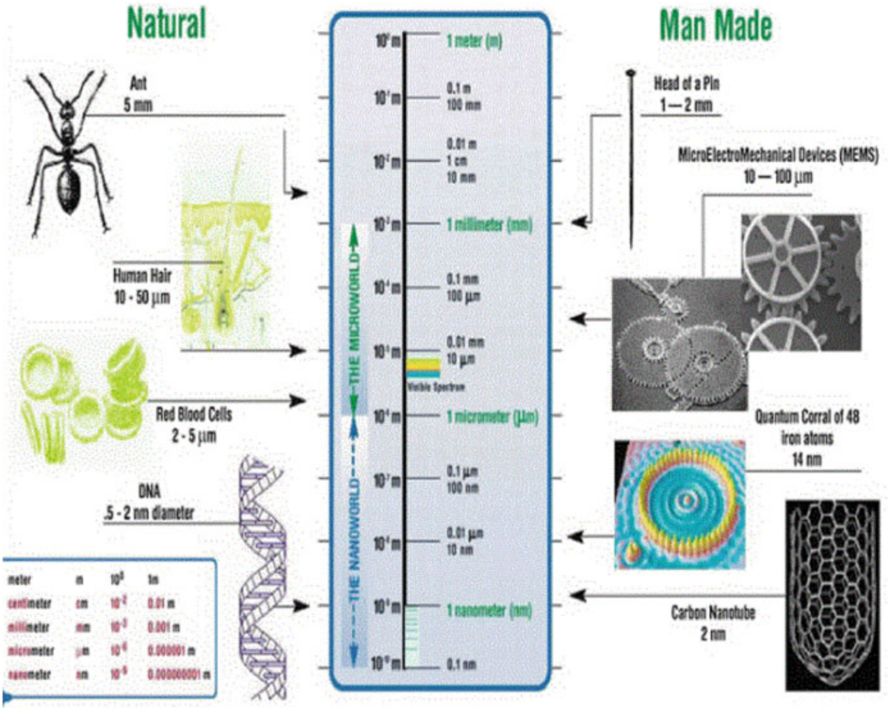


Fig. 7.3 Examples of nanoscaled materials

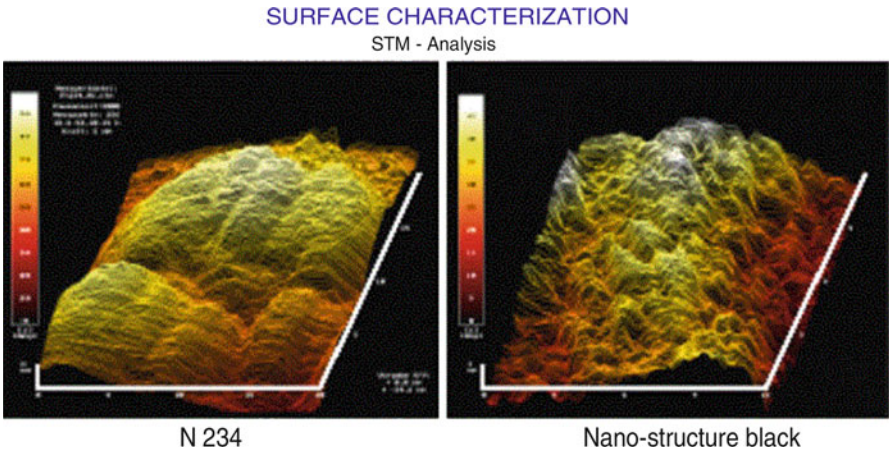


Fig. 7.4 New-generation nanostructured carbon black

between the filler and a polymer and the nanoscopic dimension differentiate polymer nanocomposites (PNCs) from traditional composites [13Cha1]. For example, nanostructured black is a family of new carbon blacks characterized by rough surface and enhanced filler–polymer interaction compared to standard ASTM black as shown in Figs. 7.2 and 7.4. The high specific surface area is one of the reasons why the nature of reinforcement is different in nanocomposites and is manifested even at very low filler loadings (10 wt%). PNCs represent a radical alternative to conventional filled polymers or polymer blends – a staple of the modern polymer industry.

7.4.1 Types of Nanofillers

The nanofillers used in polymeric nanocomposites are usually having different shapes. On the basis of this, they can be broadly categorized into the following classes as given in Fig. 7.5.

- Spherical/cubical, e.g., nanosilica, polyhedral oligomeric silsesquioxanes (POSS), nano-CaCO3, metal oxides, etc.
- Rod/fiber, e.g., synthetic whiskers, carbon nanotubes, carbon nanofibers, boehmite, sepiolite, etc.
- Sheet/platelet, e.g., layered silicates such as smectite group clays, synthetic mica, etc.

Out of these fillers, a few types of nanofillers like nanosilica, carbon nanotube, and silicates, e.g., montmorillonite (MMT), have high potential for future tire industry. Some of these nanofillers are discussed in the subsequent sections.

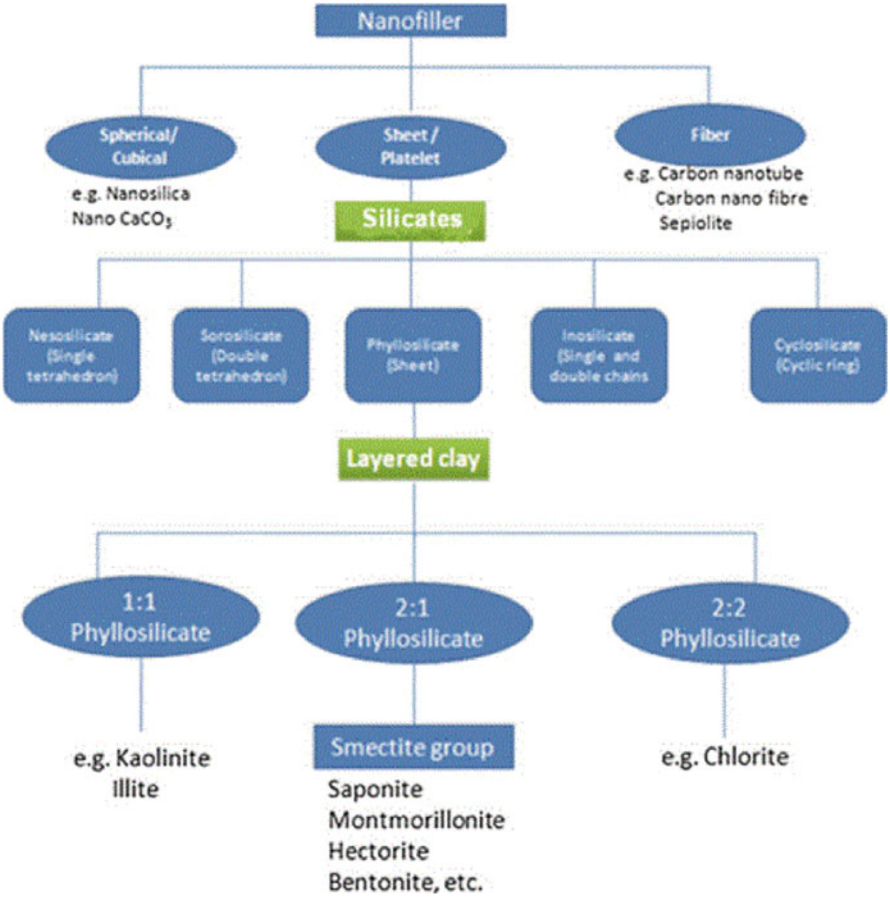


Fig. 7.5 Different types of nanofillers

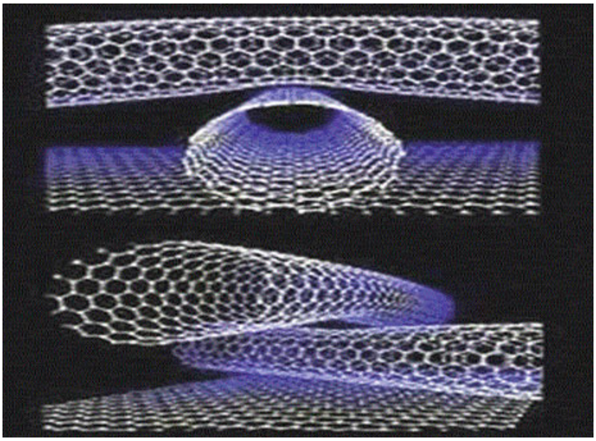
7.4.1.1 Nanosilica

Silica is one of the most abundant oxide materials in the earth's crust. It can exist in an amorphous form (vitreous silica) or in a variety of crystalline forms. Silica occurs commonly in nature as sandstone, silica sand, or quartzite. It is the starting material for the production of silicate glasses and ceramics. Nanosilica can be produced through sol–gel technique. It can be obtained in powder form. Surface treatment of nanosilica can make it organophilic and thus dispersion in elastomers can be enhanced.

7.4.1.2 Carbon Nanotube

Carbon nanotubes are promising to revolutionize several fields in material science and are a major component of nanotechnology. Nanotube has a wide range of unexplored potential applications in various technological areas such as aerospace, energy, automobile, templates, etc. Carbon nanotubes have much lower percolation threshold (i.e., lower amount is required for equivalent reinforcement). Therefore, it

Fig. 7.6 Carbon nanotubes



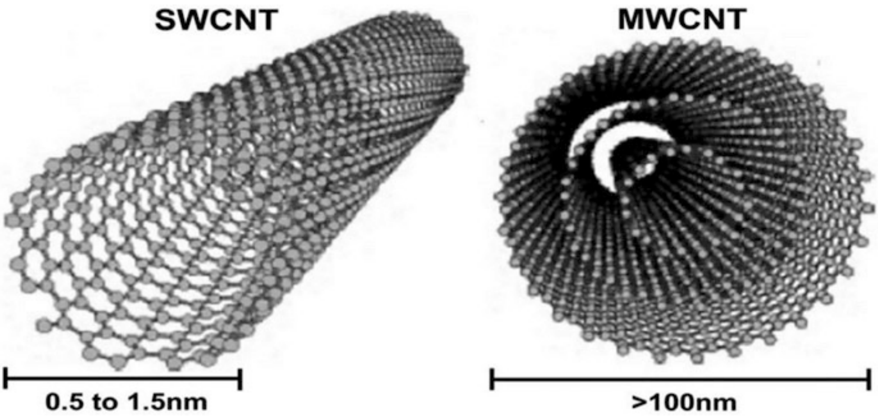


Fig. 7.7 Single-walled and multiwalled nano-carbon tube

might be possible to formulate a compound, which has all the advantages of the "green" tire by the incorporation of relatively small amount of carbon nanotubes into the silica-filled compound to achieve electrical conductivity [08Cha].

The word nanotube is derived from their size, because the diameter of a nanotube is on the order of a few nanometers and can be up to several micrometers in length.

Carbon nanotubes (CNTs) are cylindrical carbon molecules (as depicted in Figs. 7.6 and 7.7) with novel properties (like outstanding chemical, electrical, thermal, and mechanical properties and 100 times stronger than steel) which make them potentially useful in a wide variety of applications. A nanotube is a member of the fullerene structural family. Nanotubes are composed of SP2 bonds, similar to those observed in graphite, and they naturally align themselves into ropes held together by van der Waals forces.

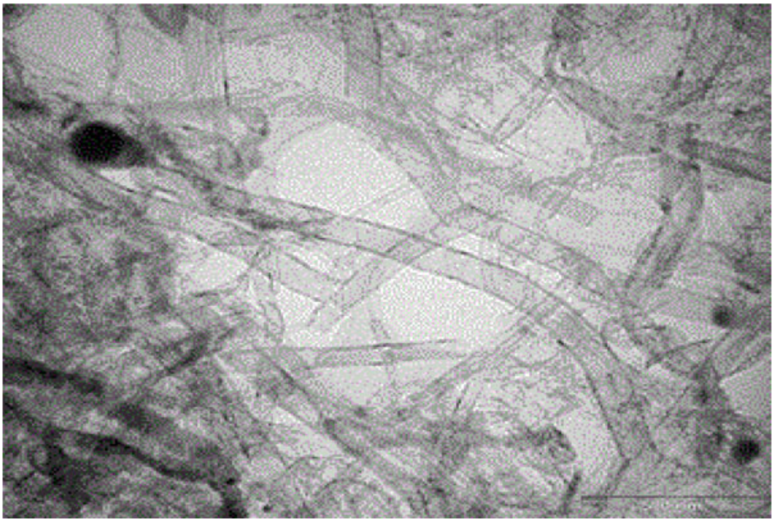


Fig. 7.8 Carbon nanofiber

7.4.1.3 Carbon Nanofiber

Carbon nanofiber is another promising nanomaterial for making high-performance polymeric nanocomposites (Fig. 7.8). Normally, carbon nanofiber having diameter in the range of 20–80 nm and more than 70 % graphitization is used in making polymeric nanocomposites. A very low level of loading of such fiber provides dissipation of charge for electrostatic painting in automobiles [01Pat].

7.4.1.4 Silicates

The silicates are the largest, the most interesting, and the most complicated class of minerals found so far. The basic chemical unit of silicates is the $(SiO_4)^{4-}$ tetrahedron. They can form as single unit, double units, chains, sheets, rings, and framework structures. In the recent years, polymer/layered silicate (PLS) nanocomposites have attracted great interest because they often exhibit remarkable improvement in materials' properties when compared with virgin polymer or conventional micro and macro composites. These improvements can include high modulus, increased strength and heat resistance, and decreased gas permeability. On the other hand, there has been considerable interest in theory and simulations addressing the preparation and properties of these materials. They are also considered to be unique model systems to study the structure and dynamics of polymers in confined environments. The field of PLS nanocomposites has gained momentum strongly during the last decade.

The silicates are divided into the following subclasses, not by their chemistry, but by their structure:

- Nesosilicates (single tetrahedrons)
- Sorosilicates (double tetrahedrons)

- Inosilicates (single and double chains)
- Cyclosilicates (rings)
- Phyllosilicates (sheets)
- Tectosilicates (frameworks)

The layered silicates mostly belong to the phyllosilicate subclass which is commonly used in the tire industry.

7.4.1.5 Layered Clays

Layered clays are minerals that assemble regularly with the unit crystalline layer, usually at the nanoscale. A layer of clay mineral is about 1 nm in thickness and consists of platelets of around 100 nm in width, representing filler with a significantly large aspect ratio. Layered clay can be classified according to the unit and ratio of crystal types they possess. These are classified as follows:

(i) 1:1 type – its unit crystal is composed of one crystal sheet of silica tetrahedron combined with one crystal sheet of alumina tetrahedron, e.g., kaolinite, illite, etc.
(ii) 2:1 type – its unit crystal is composed of two crystal sheets of silica tetrahedron with one crystal sheet of alumina tetrahedron in between, e.g., montmorillonite (MMT), saponite, bentonite, hectorite, etc.
(iii) 2:2 type – its unit lamellar crystal is composed of four crystal sheets in which crystal sheets of silica tetrahedron and alumina or magnesium octahedron are alternately arranged, e.g., chlorite.

However, the smectite group (2:1) clays are the mostly used nanofillers in polymers. Out of these, MMT has grabbed the utmost attention because of its natural abundance and ease of organic modification to promote dispersion in polymer matrices.

Structure and Properties of Montmorillonite (MMT)

Montmorillonite belongs to the 2:1 type of phyllosilicate group. The general formula of MMT is $[(Na,Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2\text{-}nH_2O]$. One layer of MMT consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of alumina. Isomorphic substitution occurs when some atoms in the crystal structure are replaced with other atoms with different valence electrons. Montmorillonite can absorb water between the charged layers because of the weak binding and the large spacing between the layered sheets, and it is therefore a member of a group of water-expandable clay minerals known as smectites or smectite clays.

It can be understood that the layers of MMT are connected by weak van der Waals force of attraction and are arranged themselves in stacks with some gap in between, often termed as “interlayer” or “gallery spacing.” The isomorphic substitution of metal ions generates an excess of negative charge, and the quantity of this governs the characterization of the clay type and in general termed as cation exchange capacity (CEC) of the clay. In natural MMT, this charge is balanced by the group I and II metal cations (Na+, Ca++, etc.) in their hydrated form and that is why it is compatible with hydrophilic polymer. But dispersion of such clay into hydrophobic

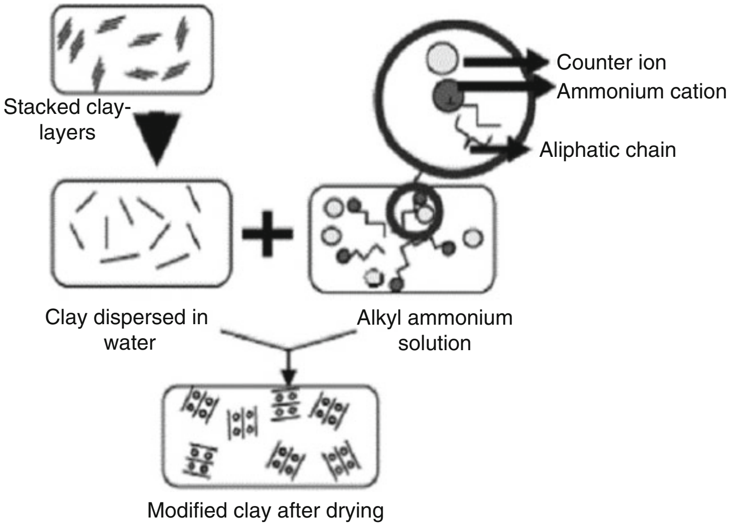


Fig. 7.9 Organic modification of nanoclay [08Mai]

polymeric matrix is a difficult task. To alleviate this problem, MMT can be organically modified by exchanging the inorganic cations such as Ca++, Na+, and K+ (those exist in the galleries of silicate layer) with quaternary alkyl ammonium ions resulting in better compatibility of the silicates with the polymer matrix [02Bec, 03Plu, 07Kim].

Organically Modified MMT Clays

Hydrophilic nature of clays hinders their good interaction with organic polymers. Therefore, surface modifications of clays are necessary to render them hydrophobic in order to achieve a better interaction of clay surface with the polymer matrix [08Mai]. Figure 7.9 represents the process of organic modification of nanoclay. The MMT-based organically modified clays are classified according to the structure of the intercalants (surfactant – quaternary alkyl ammonium ion) used for this modification as well as the cation exchange capacity (CEC).

7.4.1.6 Polyhedral Oligomeric Silsesquioxane (POSS)

Polyhedral oligomeric silsesquioxane is a hybrid nanostructured macromer (shown in Fig. 7.10). It has been used in the last decade for preparation of polymeric nanocomposites. Its versatile chemistry, which lends it for almost infinite chemical modification, sets it apart from other nanostructured fillers like nanoclays, carbon nanotubes, and carbon nanofibers. Depending on its functionality, 3-D network, bead, or pendant-type POSS-based polymeric nanocomposites can be synthesized. These composites have the potential to be designed for products with specific nanostructures for specific end-use applications.

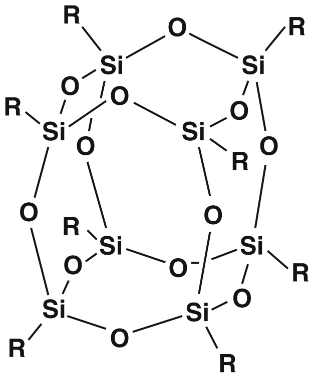


Fig. 7.10 Molecular structure of polyhedral oligomeric silsesquioxane (POSS)

The crystal structure and morphology of inorganic–organic hybrid POSS nanoparticles consist of an inorganic core of silicon and oxygen and outer organic attachments of alkyl groups. These molecules self-assemble to form a hexagonally packed structure. Alkyl attachments are accommodated within the interstices of the hexagonal lattice. This is the reason for the disorderness which is observed in polymer–POSS nanocomposite materials such as those formed by copolymerization.

7.5 Applications of Polymeric Nanocomposites

7.5.1 Automotive Tire

Among all the polymer-based automotive components, tire is the most important one. A tire must deliver high traction on dry as well as wet roads, commonly called as wet and dry grip. This high traction force between tread and road is necessary for avoiding slippage while running on the road. Again, a tire must exhibit low wear and good durability; the abrasion resistance of the tread compound should be as high as possible to achieve better mileage. With regard to the fuel consumption, rolling resistance is another important parameter, which is related mainly to the tread compound. All these three parameters (traction, abrasion resistance, and rolling resistance) are interrelated under a common head popularly known as “magic triangle” (Fig. 7.11). The name is so because all the three properties are conflicting and interdependent, and always a better balance among the three is required. From the beginning of tire manufacturing, researchers have been keen to get the best balance of the magic triangle. Filler is one of the key ingredients to balance these properties. Reinforcing fillers such as carbon black and silica individually or in combination with special chemicals are incorporated into the tire to enhance the mechanical properties as well as to improve the magic triangle. To achieve a better solution, the concept of nanotechnology is being introduced slowly in the tire technology (Fig. 7.12).

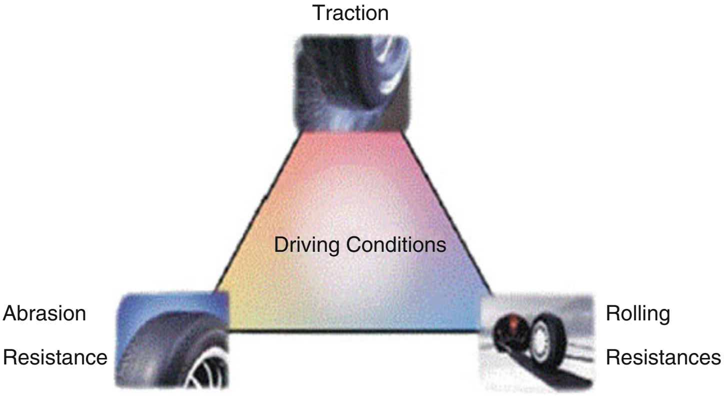


Fig. 7.11 Magic triangle of tire performance

Fig. 7.12 Schematic illustration of a modern nanostructure-based tire for cars [08Das, 10Zho]

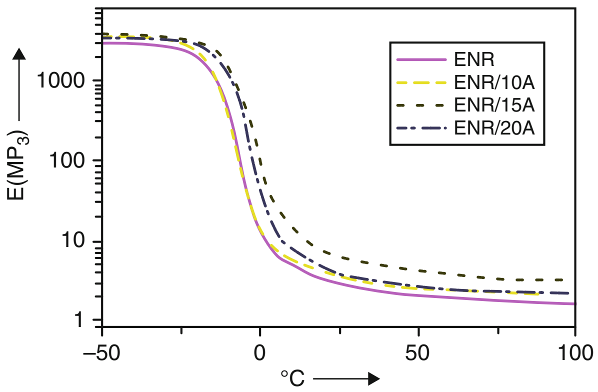
Many leading tire manufacturers are now developing engineered composites to further extend the life of tire. Pirelli has announced in 2004 the first application of nanomaterials in their winter segment [06Cha]. Carbon black with small particles (including nanoparticles) has long been mixed with rubber to improve the wear and strength of the tire. Cabot, one of the world's leading carbon black producers, successfully tested "PureNano" silica carbide nanoparticles designed by Nanoproducts Co. of Longmount Colorado [www.azonano.com/Details.asp'; Article ID = 1351]. When it is added to a tire, "PureNano" particles reduce abrasion by almost 50 % – a simple improvement that if widely adopted should help tire to last twice long and thereby significantly reduce the need for new tire/rubber. Aeromet Technologies, Inc. of Sandy, Utah [www.voyle.net/Nano%20biz/NanoBiz. 004], crafts a cleaner process for bonding steel tire cords to rubber during tire manufacturing. Their new bonding material based on nanoparticles will eliminate the usage of hazardous chemicals such as cobalt and cyanide. Strong and lightweight rubber–carbon nanotube composites are coming strongly in the market [06Str]. In addition to these, different types of nanocomposites find their use in tire industries (shown in Fig. 7.12). A few such types of nanocomposites are discussed here.

7.5.1.1 Epoxidized Natural Rubber/Organoclay Nanocomposite

Epoxidized natural rubber (ENR) is such a rubber which has combined properties of natural rubber and a polar rubber. The epoxidized natural rubber (50 % epoxidation) with different grades of nanoclay (cloisite 10A, 15A, 20A) was mixed to prepare nanocomposites. Nanoclay shows a significant reduction of scorch time and considerable increase in maximum torque compared to conventional ENR compound. ENR/clay nanocomposites have higher storage modulus which indicates the higher polymer–filler interaction of the composite and consequently better physical properties [06Cha, 08Wan] as shown in Fig. 7.13.

Tan delta values of the composites were found significantly reduced at high temperature which signifies lower rolling resistance and better fuel economy for the ENR/clay nanocomposites. Thus, ENR/organoclay nanocomposite can be used as tread compound in the future for making high-performance tire.

Fig. 7.13 Variation of storage modulus as a function of temperature [06Cha]



7.5.1.2 SBR/Clay Nanocomposite

SBR/clay nanocomposites were made to get significant dispersion of nanoclay in polymer matrix that can be characterized by X-ray diffraction. It is observed that addition of up to ten parts of nanofillers in SBR improves tensile strength more than 40 %. It also improves the dynamic properties of the compound significantly. But the effect of nanoclay on SBR is greatly dependent on its concentration, and it is observed that up to 6 phr of nanoclay provides significant improvement of mechanical and dynamical properties [11Jee]. The effect of nanoclay in SBR can be enhanced significantly by adding the carbon black. It is observed that addition of carbon black in SBR/clay nanocomposite gives tremendous improvement in the mechanical properties [08Jee, 11Jee]. Nanoclay in combination with carbon black in SBR–BR-based passenger car tread shows a considerable reduction in abrasion loss [07Sum].

7.5.1.3 Butyl/Clay Nanocomposite

The excellent air retention property of butyl (IIR)/halobutyl (XIIR) is very well known in tire industries. These rubbers are extensively used in inner tube (IIR) of tube-type tire and in inner liner (XIIR) in tubeless tire. There are also some other elastomers which are not used in tire industries, but have very good and even better air retention properties, like epichlorohydrin rubber (ECO), polysulfide rubber (TM), and polyurethane (PU). There are also some elastomers, like nitrile rubber (NBR) and ethylene/acrylate copolymers (EAM), which provide moderate air retention properties.

Using butyl as elastomer and clay as filler with high aspect ratio, the air retention properties could be improved to the level of 50 times better than that of the normal butyl compound. Using such filler, therefore, the inner liner gauge or gauge of inner tube could be reduced for identical condition of services [10Cha].

The reason for the air barrier properties is that with carbon black as filler, the passage of air is faster because of the spherical nature of the filler. With needle-shaped filler in nanocomposite, the same air will take longer time to travel due to the flat shape of the filler (Fig. 7.14).

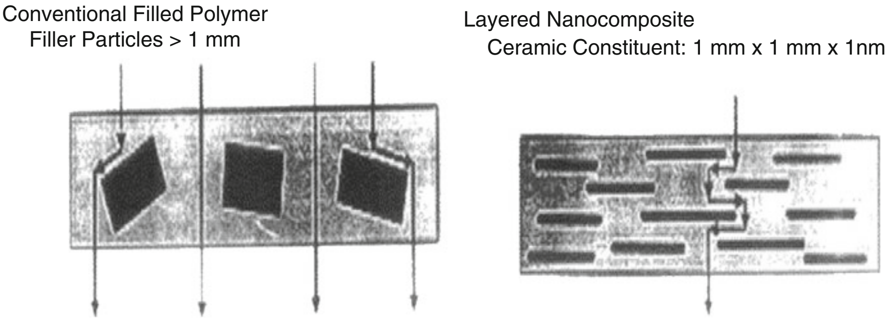


Fig. 7.14 Passage of air in carbon black-filled compound and nanocomposite

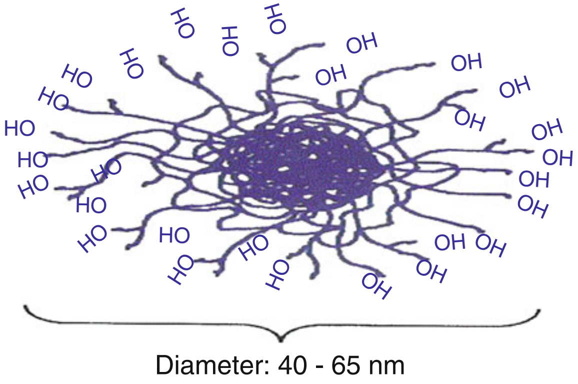


Fig. 7.15 General model of nanorubber [11Fra]

7.5.1.4 Nanorubber

Nanorubber was developed jointly by Dr. Werner Obrecht and Lanxess, with a series of patents on the production process and on the applications. It is defined as nanorubber because it is characterized by a chemical nanostructure whereby the rubber particles have dimensions of 40–65 nm (shown in Fig. 7.15). The nanorubber has been designed with a highly cross-linked particle core, and consequently the particle morphology is not destroyed by high shear. Additionally, due to a high degree of core cross-linking, the compounding ingredients such as oil, sulfur, and accelerators are not absorbed by the core. Moreover, owing to chemical composition and cross-link density, the particle core exhibits a specific Tg, which influences temperature-dependent damping characteristics of vulcanizates (i.e., rolling resistance and wet traction). More precisely, when the nanorubber particles are dispersed in a conventional polymer matrix, they form a separate phase in the continuous phase of the polymer matrix and hence behave exactly like filler. Moreover, the particle size of nanorubber is comparable to that of N550 and N660 grades of carbon blacks.

As disclosed in numerous patents on nanorubber, the development of this new material started from the observation that high levels of microgel in old emulsion SBR (E-SBR) and old emulsion polymerized BR were giving to the resulting vulcanizates high-rebound resilience at 70 °C (158 °F), which corresponds to low rolling resistance in tire treads and low-rebound resilience at 23 °C (73.4 °F), ensuring high wet skid. While the vulcanizates with microgel had good dynamic properties, the drawback is that there are adverse effects on mechanical properties, such as tensile strength, tear resistance, and wear resistance properties [11Fra].

To keep the good dynamic properties offered by the polymer gel, but simultaneously compensate the low ultimate mechanical properties, nanorubber was developed with a precise and tailor-made chemical structure as shown in Fig. 7.15. It should be added to the common polymer matrix on top of the 100 phr of the rubber content – really just as a filler. Additionally, the nanorubber, as filler, has been designed to be reactive with polar fillers. For this reason, the extremities of the polymer chains of the nanorubber are endcapped with hydroxyl groups to permit the linkage between the surface of the rubber nanoparticles and the silica surface in the presence of silane [11Fra].

The nanorubber can be used as filler in a common carbon black-filled compound without the usage of silica or other polar fillers and without the use of silane coupling agents.

7.5.1.5 NR/BR/SBR–Nano Calcium Carbonate Composite

The application of an active nano-calcium carbonate in tire was experimentally investigated. The physical and processing performance of rubber compounds is improved by adding 5–8 phr active nano-calcium carbonate in sidewall and carcass ply of tire together with proper loading adjustment of carbon black and oil in compound formulation. In tire tread, with the addition of 4 phr active nano-calcium carbonate in the compound, the tear strength was improved while maintaining the same abrasion resistance and other physical properties with better extrudability. The addition of active nano-calcium carbonate in tire compounds can reduce the production cost with better productivity [Liu].

7.5.2 Thermoplastic-Based Nanocomposites

Thermoplastic-based nanocomposites filled with nanoclay, carbon nanotubes, and nano-carbon fiber have high potential for automotive applications. It is because of the fact that low loadings of such fillers do more than heavier loadings of the other fillers. Nanoclay with thermoplastics or carbon nanotubes with thermoplastics and thermoset materials can provide dramatically different properties for improving charge dissipation, surface quality, stiffness – toughness balance – and reduce permeability, improve thermal stability, and reduce part weight. These composites have potential applications in bumper facias, fuel lines, body panels, and instrument panels. TPO-based nanocomposites increase stiffness and reduce density, and they also improve scratch resistance properties and reduce thermal stability. TPO for bumper facias generally contains 60 % PP (15 % atactic homopolymer, 15 % isotactic homopolymer, 30 % copolymer), 30 % elastomer (EPDM), and 10 % talc.

Addition of carbon nanofiber in sheet-molded compound (SMC) improves charge dissipation by eliminating conducting priming of parts for electrostatic painting in body panels. It also retains class "A" surface quality. Another opportunity with carbon nanofiber is to reduce calcium carbonate loading in thermoplastics for improved toughness and thinner panels (lighter weight).

7.5.3 Automotive Coatings

7.5.3.1 Highly Scratch-Resistant Clear Coat Containing Inorganic Nanofillers

It has been found that incorporation of nanoparticles such as Al_2O_3, SiO_2, ZrO_2, and TiO_2 into a clear coat matrix could significantly enhance the scratch resistance [08Ame, 08Gro, 10San, 10Tah, 11Bau]. Ceramic nanoparticles have been found as appropriate hardening materials to significantly improve clear coat hardness and therefore scratch resistance. However, the improvement cannot be easily obtained when the particles are poorly dispersed. The inorganic fillers do not have intrinsic affinity to organic phase. These lead to phase separation and aggregate formation. The aggregated particles ($>$100 nm) depreciate clear coat properties especially the optical clarity. Attempts have been carried out to solve this problem by surface modification of fillers with organosilanes to render them hydrophobic and thereby improve their dispersibility into the polymeric matrix. The surface modification not only can influence dispersibility but also can result in stronger physical/chemical interfacial adhesion between particles and the matrix [10Tah]. Different factors such as the particle chemistry, size, shape, and surface modification may be influential for the effects of nanofillers on the scratch resistance of a clear coat. It has been demonstrated that nanoparticles could improve clear coat properties in different ways. Inorganic nanoparticles have hardness and elastic modulus greater than organic polymers (Fig. 7.16). However, it has been shown that greater hardness does not necessarily guarantee clear coat scratch resistance. There are problems with highly increased clear coat hardness. For example, when the applied forces are greater than the critical force, it leads to fracture-type scratches. Increasing coating hardness can also result in an increase in clear coat brittleness and, therefore, reduction of other properties like flexibility. To overcome this problem, attempts have been carried out to obtain tough clear coat in the presence of nanoparticles. Results obtained in recent researches show that nanoparticles could influence cross-linking density of the clear coat by affecting curing reaction. Nanoparticles with organosilane modifications include functional groups with high capability of reacting with functional groups of resins. As a result, some chemical bonds between resin and hardener (curing agent) will be replaced by the bonds created between

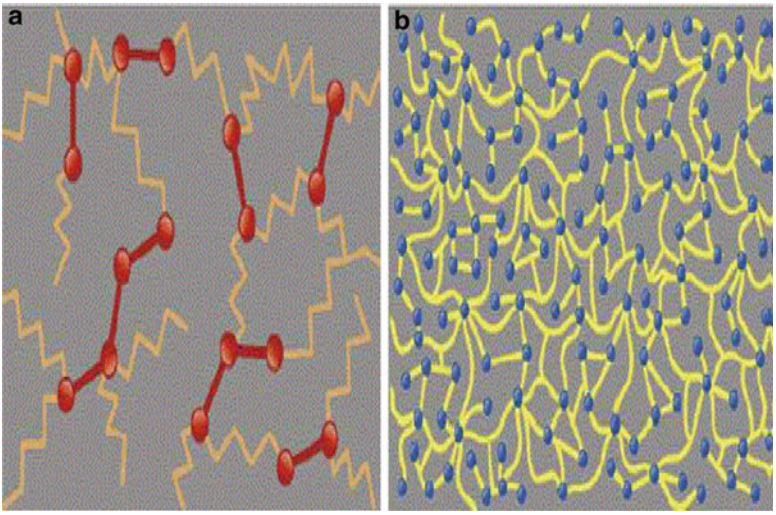


Fig. 7.16 Schematic illustrations of the chemical structures of the conventional coating consist of resin/cross-linker (**a**) and inorganic nanoparticles loaded paint (**b**)

particle/hardener and/or particle/resin. This results in a decrease in the cross-linking density of the clear coat. On the other hand, nanofillers enhance the hardness and elasticity. These two phenomena result in clear coat toughness improvement in the presence of nanoparticles. A tough clear coat can resist abrasive condition and show less fracture behavior [08Ame, 08Gro, 10San, 10Tah].

Highly Scratch-Resistant Clear Coat Using Sol–Gel Method

Nanofiller-embedded clear coats show enhanced scratch and wear resistance. However, the clear coat transparency will be influenced as a result of nanoparticles aggregation. Obtaining appropriate dispersion needs surface modification as well as using different dispersing techniques. In situ process of inorganic phase formation inside organic matrix using sol–gel technique has been considered [03Her, 03Pre, 11Ram]. Organic/inorganic precursors can be used to produce in situ silica network in the matrix. These precursors, either as network former, such as tetraethyl orthosilicate (TEOS), or network modifier, such as methacryloxypropyltrimethoxysilane and glycidoxypropyltrimethoxysilane (GPTS), can be introduced to the main polymeric film former to obtain so-called hybrid nanocomposite films. This process includes precursor hydrolysis and self-condensation reactions. The hydrolyzed precursors could be cross-linked with the organic coating matrix by reacting with polyol and other curing cross-links such as amino or isocyanate compounds in the automotive coating formulation. In this way, a hybrid nanocomposite containing organic/inorganic phases can be obtained (as given Fig. 7.17). The organic phase presented in the hybrid nanocomposite can be responsible for the adhesion and

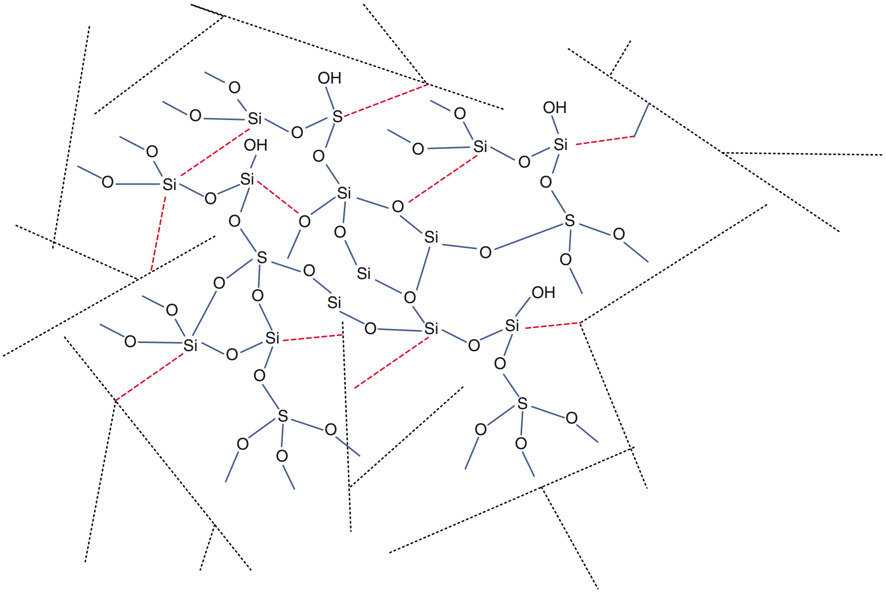


Fig. 7.17 Schematic illustration of a sol–gel-based automotive clear coat containing organic/inorganic precursors [10Ram]

flexibility, and the inorganic phase can help coatings resist mechanical damages [10Ram].

7.5.4 Scratch-Resistant Polymeric Glasses

Nowadays, fuel consumption of a car is an important factor for both car manufacturers and consumers. Request for producing cars with lower fuel consumption has been enormously popular in recent years. Reducing the weight of the cars is one of the ways to achieve this target. The car weight can be significantly reduced by replacing heavy glass parts (i.e., head lights and windows) by light polymeric glass sheets [11Yah]. One of the most commonly used kinds of glass polymers is polycarbonate which has excellent impact strength and high toughness and is lightweight. Polycarbonates have been already used in light covers and lenses. However, polycarbonate has limited scratch/abrasion and chemical resistance together with the tendency to yellowing when it is exposed to UV light for long term. Glass is a hard material having excellent scratch resistance. However, it has higher weight and lower impact strength compared with polymeric glasses. Washing (both automatic car wash and hand wash) and sand/dust particles presented in air are main causes of scratching polycarbonates glass parts. This may result in a significant reduction in head lights transparency and therefore light scattering. Attempts have been carried out to solve the problem. Two methods have been sought for this purpose. Producing polycarbonate polymeric glass parts by embedding nanoparticles into it and/or using acrylate or polysiloxane paints over the head light. Aluminum oxide nanoparticles are also used in the coatings composition in order to make it hard enough to resist scratch and abrasion. This coating is highly transparent due to the small size of the filler particles and their fine distribution [90Bri, 11Yah]. Embedding nanosized silica particles into an organic modified siloxane-based coating results in nanocoating for automotive glazing application. This coating can produce various properties for the plastic glazing like hydrophobic/anti-smudge, infrared (IR) and ultraviolet (UV), and shielding and antifogging behavior. The schematic illustration of a nano-enhanced automotive plastic glazing is shown in Fig. 7.18.

The average thickness of the nano-embedded coating used for polycarbonate is approximately 1 mm. Different nanocoating layers are responsible for anti-scratch/easy-to-clean/antifogging and UV stabilization of polycarbonate plastic glazing. To this end, nanoparticles such as TiO_2, SiO_2, and Al_2O_3 for abrasion resistance improvement, TiO_2 and ZnO for UV protection, sol–gel-based TiO for antifogging behavior, and TiO_2 for easy-to-clean properties are used [90Bri, 11Yah]. In premium optical glazing like glass panes, it is necessary to use coatings with extremely high scratch resistance. To this end, attempts have been made to apply hard materials over the polymeric glass through gaseous phase. Using physical vapor deposition (PVD) and chemical vapor deposition (CVD) procedures as well as plasma polymerization, a highly cross-linked nanometric polymeric layer containing inorganic components can be obtained. Producing highly scratch-resistant polymeric glass using these

Fig. 7.18 Modern automobiles equipped with nanostructured polymeric glasses for roof, windows, and cover light

techniques opens new possibilities for designing transparent rooftops and car body shell parts.

7.5.5 Weather-Resistant Automotive Coatings

Recently, various nanoparticles such as zinc oxide, iron oxide, cerium oxide, titanium oxide, and silica have been incorporated into conventional polymeric coatings to enhance their resistance against sunlight. Nanoparticles, possessing a high surface area for absorbing the harmful part of sunlight (ultraviolet part), prevent the coatings from weathering degradation. Since they are inorganic and particulate, they are more stable and nonmigratory within an applied coating. So, they present better effectiveness and longer protection.

As mentioned, TiO_2 nanoparticles are effective to fight against UV rays and can protect the coating against weathering. However, these nanoparticles especially can exert strong oxidizing power and produce highly reactive free radicals and degrade the coating in which it has been incorporated. Thus, photocatalytic activity of TiO_2 nanoparticles has to be controlled. For this purpose, treatment of nanoparticles by different techniques such as silane agents not only suppresses photocatalytic activity of TiO_2 nanoparticles but also offers clear advantages like simplicity, low cost, and processing at low temperatures. It has also been demonstrated that surface modification of TiO2 nanoparticles with aminopropyltrimethoxysilane (APS), considerably, has reduced photocatalytic activity of nanoparticles and enhanced the weathering resistance of a polyurethane coating [11Mir]. In various researches, it has been shown that zinc oxide nanoparticle can be an effective option to nearly completely screen the UV rays and protect the coating [08Low, 11Ram]. In an attempt to improve the UV resistance of an aromatic polyurethane-based automotive electro-coating, nano-ZnO particles were used. The results obviously illustrated that the presence of nano-ZnO particles could decrease the photodegradation tendency of the film and protect it against deterioration [11Ras].

7.5.5.1 Nanomaterials to Protect Weathering Due to Biologicals

Although humidity and sunlight are the two main factors which degrade automotive coatings, other environmental factors, e.g., those originated from the biological sources, can have a spoiling impact on the appearance of a car body during its service life [09Ram]. It was also found that the most important factors governing the degradation are the coating chemical structure at surface and adhesion between coating surface and biological materials. Therefore, it was thought that any modification which could be able to alter both surface chemistry of the clear coat and adhesion would be an ideal option to fight bio attacks. This idea was proved by a series of experiments. It was demonstrated that modification of clear coat with a functional silicone additive significantly improved the coating performance against bird droppings and tree saps [12Ram].

According to these new findings, creating a clear coat with nonstick and superior water repellency properties would significantly reduce the failure of coatings caused by biological materials. Ultra-hydrophobic self-cleaning coating which is produced by nanotechnology is a powerful approach for this purpose. Contaminants on such surfaces are swept by water droplets or adhere to the water droplet and are removed from the surface when the water droplets roll off. Although these types of coatings for automotive glasses have been already commercialized, their development for automotive paints is in progress.

7.5.6 Smart Windows Based on Electrochromism

It has become an essential requirement to provide a secure and comfortable condition for driver and passengers in any vehicle. To this end, automotive experts strongly believe that all types of energy like sound, light, and heat which enter the car body have to be controlled. Recent progresses in polymer and different types of dichromic technology have allowed the development of smart glasses which intelligently control solar radiation transmission and modulate glare, increasing passenger comfort and safety. Among different kinds of smart glasses, electrochromic (EC) ones are very important. EC materials based on nanotechnology alter their optical characteristics (darkness/lightness) when a small electric potential difference is applied. They are suitable for a wide range of applications. They can be employed in different parts of an automobile like for energy-efficient windows, antiglare rearview mirrors, sunroofs, and displays.

DuPont has developed an EC device based on an organic polymer technology to control light transmission in automotive applications. In comparison with current EC technologies, this not only is less complicated, but also it can be used in rigid and flexible forms, large sizes, and curved shapes. Target markets of this technology in automotive include sunroofs, mirrors, instrument clusters, windshield shade bands, side lights, and back lights. It is predicted that the market for smart windows will become a billion-dollar one by 2016 and will be doubling by 2018. The automotive market provides the next largest source of smart window opportunities for glass suppliers, after the architectural markets.

7.5.7 Automotive Fabrics

It is a part of commercial strategy for car manufacturers today to improve the safety and convenience aspects of automobiles. Textiles, especially fabrics, as the main substances in designing the interior parts of a vehicle are very important. They are utilized in various parts such as interior panels for doors, pillars, seats coverings, paddings; parts of the dashboard, cabin roof, boot carpets; and headliner, safety belts, airbags, etc. Nanotechnology as a powerful tool has aided the auto-manufacturers to reach their goals in a short period of time. The most important properties of automotive fabrics which have been modified by the aid of nanotechnology include antimicrobial, self-cleaning, and fire retardancy.

7.5.7.1 Antibacterial Fabrics

Textiles can grant an appropriate environment for microorganisms' growth especially at proper humidity and temperature in contact with the human body. The rapid and uncontrolled fast thriving of microbes can lead to some serious problems. In commercial viewpoint, antibacterial automotive textiles based on nanotechnology are beginning to enter the market. For example, Tencel™ material based on nanofibrils of cellulose was produced by Lenzing. It has a combination of properties and in particular antibacterial properties which reduces growth of bacteria. This product has been introduced to the market as a good candidate for seat covers of car.

7.5.7.2 Hydrophobic Surfaces and Anti-Stain Textiles

Carbon nanotube, silica, and fluoro-containing polymeric nanoparticles were applied to nylon, cotton, and polyester fabrics in the form of a coating for making superhydrophobic surfaces [Moh]. In these research works, they could achieve artificial lotus leaf structures. Opel Company was the first manufacturer in the world to equip seating upholstery of the car named "Insignia" with the nanogate coatings that repel dirt and liquid staining.

7.5.7.3 Flame Retardancy

Recently, polymer nanocomposites offering significant advantages over conventional formulations have received many attentions in the field of flame retardancy. Nanoparticle fillers are highly attractive for this purpose, because they can simultaneously modify both the physical and flammability properties of the polymeric matrices. Layered silicates (clay) and carbon nanotubes (CNTs) are two main nanostructured materials that have attracted the attention of scientists to promote fire performance of polymeric substrates like textiles [04Bel, 10Kil]. The nanomaterials make fabrics less ignitable and self-extinguishable when the flame is removed. Since flame retarding mechanisms of clay and CNTs are different, significant synergism happens when they are introduced to textile together, leading to a much more efficient approach to improve the flame retardancy. In recent studies, polyhedral oligomeric silsesquioxane (POSS) compounds have been utilized as fire-retardant agents. In a series of experiments, Bourbigot and coworkers introduced POSS nanoparticles in polypropylene yarns, cotton, and knitted polyester and showed that the time to ignition increased significantly as a result of the presence of nanoparticles [05Bou].

7.5.8 Ultra-Reflecting Layer for Automobile Mirror

7.5.8.1 Mirrors with High Optical and Self-Cleaning Properties

New generation mirrors and headlights used in cars are based on glass and polymeric components with high optical quality and efficiency. Nanotechnology is employed to achieve these unique properties. For achieving this, ultra-reflecting thin layer (having thickness of less than 100 nm) based on aluminum oxide is applied over the surface of mirrors or headlights. Applying ultrathin layers over the mirrors can also make the surface resistant to fat, dirt, and water. Using chemical vapor deposition (CVD) technique, nanometric hydrophobic and oleophobic layers can be applied over the surface of mirrors. It has been found that fluoro-organic materials are able to improve hydrophobicity and oleophobicity of the surface at thicknesses of 5–10 nm. This nanometric layer could also produce smooth surface on which impurities like waterdrop, dirt, oil, and fingerprints can be easily cleaned. This ultrathin layer has high resistance against friction and makes it applicable at longer times. As it can be seen in Fig. 7.19, the layer could be chemically bonded to the surface of mirror from the side consisting anchor groups. The chemical groups at other side of the layer produce hydrophobic surface.

7.5.8.2 Antiglare Rear Mirrors

Nowadays, safety regulations for car drivers lead to produce rearview mirrors to obtain an appropriate view at dawn and dusk. This can be done by equipping glasses with functional layer composite with electrochromic properties. The optical properties of the glasses equipped with this technology will be changed by applying a certain voltage which moves the charges to intermediate layer. The incoming light will be absorbed by color centers produced by ions at the electrodes. As a result, small quantity of light will be reflected (Fig. 7.20).

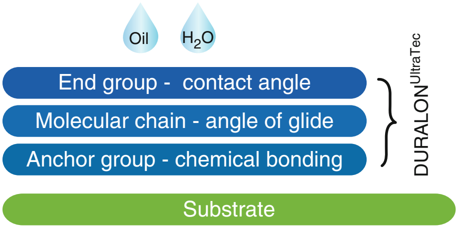


Fig. 7.19 The composition of ultra-reflecting layers used on modern mirrors

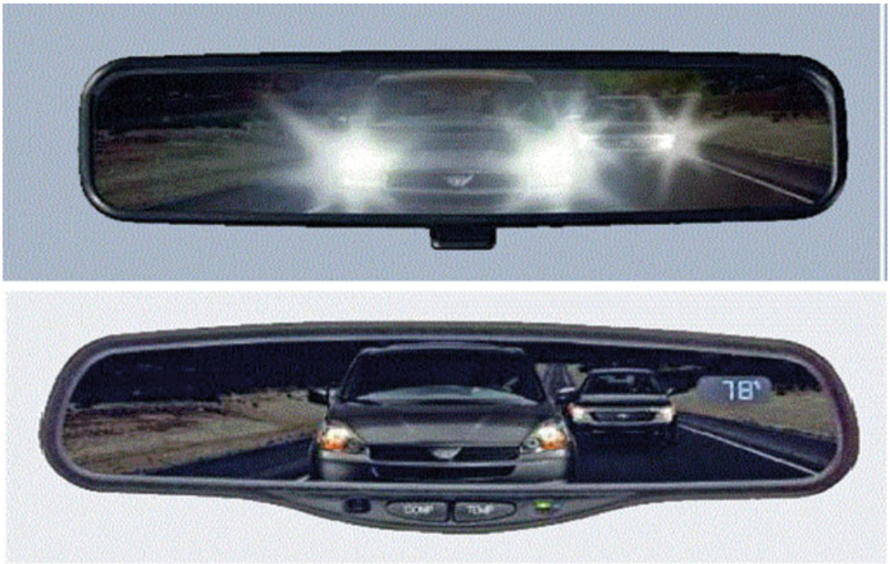


Fig. 7.20 The conventional mirrors (**a**) and modern antiglare rear mirrors for cars (**b**)

Like charging and discharging of a car battery, the glass can get back to its original properties as the pole changes. This glass equipped by a rear sensor could measure and control the glaring light of following vehicles. As soon as the glaring light disappears, the mirror gets back to original state.

7.5.9 Polymeric Electrolyte Membrane Fuel Cell

Polymeric nanocomposites also find applications in generating green and environment-friendly energy for automobiles. To replace combustion engines, different strategies and methods have been developed. Among them, electrochemical energy production/storage is the most important option owing to sustainability and being environment friendly [01Sch]. Out of these, fuel cells look more promising compared to batteries and supercapacitors. Though, there are still many challenges to be solved to have energy conversion/storage systems which could surpass combustion engines in terms of power/energy performance and cost [04Win]. Nanomaterials are finding great applications in overcoming these challenges [05Ari, 09Ser].

Polymeric electrolyte membrane fuel cell also known as proton exchange membrane fuel cell (PEMFC). These are being developed for automobile applications as well as in a variety of portable stationery applications. Automobiles powered by fuel cells are believed to have considerable markets in the near future, and it is envisaged about 80 million fuel cell vehicles will be on road by 2020. A large number of corporations are engaged in development of fuels cell or becoming strategic partners. Major companies like DuPont, Gore, SGL, 3 M, and Johnson Matthey are positioning themselves as world suppliers of PEMFC components. The primary components of a PEMFC are an ion-conducting electrolyte, a cathode, and an anode. The basic cell consists of a proton-conducting membrane, such as perfluorinated sulfonic acid polymer, sandwiched between two platinum-impregnated porous electrodes. The use of fuel cells is described in the following paragraphs.

At the present conditions also, one can drive a car powered by some classes of fuel cells (PEMFCs). But there are still some challenges associated with employing them which are mostly high cost, fuel supply/storage, and service lifetime. Generally, the fuel choice is hydrogen and oxygen which finally combined to produce energy and exhaust water. Hydrogen supplication, refueling infrastructure, and storage of hydrogen are still ongoing challenges [07Cha]. There has been considerable research to develop new materials enabling storage of hydrogen at high concentration at not too high pressure and too low temperature. Initial interest was focused on metal hydrides through chemisorptions of hydrogen. However, efforts were quite unsuccessful to synthesize metal alloys reaching to theoretical limit (~8 wt%) unless some promising results were reported for nanosized metal (oxide) composites [05Ari]. Metal alloys such as LaNi, TiFe, and MgNi are generally expensive and in all cases are heavy which makes commercialization of products dealing with mobile applications problematic. Novel nanoporous materials, metal organic frameworks (MOFs), have been the center of attention for gas adsorption. These materials are product of reaction of metals ions with rigid organic molecules. Due to exceptionally high surface area and tunable chemical structure of MOFs, high potential for high enough H_2 uptake is envisioned. In September 2011, Daimler introduced a concept vehicle, Mercedes-Benz F125, which was pictured to be derived by 2025 (http://media.daimler.com). The most interesting technology of this conceptual car is its source of energy which is hybrid of Li-S battery and hydrogen fuel cell.

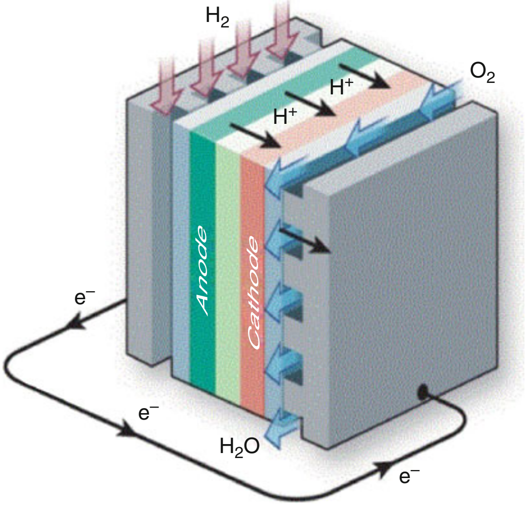
The manufacturer claims one will be able to derive up to 1000 km with maximum speed of 220 km/h before it is needed to be refilled.

Although interest to fabricate solid-phase hydrogen reservoir using CNTs are now quenched, emergence of the carbon-based thinnest materials, i.e., graphene, again revived hopes to have carbon-based hydrogen storage tanks [07Par, 08Dim, 10Bur]. In fact, as the H_2 storage mechanism in carbon nanostructures relies on physical absorption on graphenic surface, the hydrogen uptake is proportional to specific surface area of nanostructure which reaches ultimate value for carbon nanostructures in graphene (2630 $m^2g/1$) [08Dim]. Research on developing high surface area graphene-based materials is ongoing. However, more time requires confirming whether graphene-based nanoporous materials are able to solve the mystery of the hydrogen storage or not [11Sub].

The expensive constituents of fuel cells associated including the catalyst and electrolyte membrane are the origin of high cost of fuel cells [01Ste]. In addition, performance and lifetime of these classes of fuel cells (PEMFC) can be remarkably improved by nanoengineering of the catalyst and electrolyte membrane.

Principally, fuel cells (PEMFCs) operate with a polymeric electrolyte membrane which is sandwiched between cathode and anode that separate the fuel (hydrogen) from the oxidant (air or oxygen) as depicted in Fig. 7.21. The performance of these

Fig. 7.21 Basic structure of hydrogen fuel cell in which hydrogen splits into electron and proton at anode and at cathode; protons reduce oxygen exhausting water finally [10Tol]



low-temperature fuel cells is mostly limited by oxygen reduction reaction (ORR) [05Ari]. The current generation's fuel cells utilize platinum (Pt)-based catalyst for both the oxidization of fuel and reduction of the oxygen (09Gre). Today, Pt–carbon catalyst which are widely used in PEMFCs are nanoparticles of Pt decorated on carbon support (e.g., carbon black) [09Gre]. Pt nanoparticles' activity increases as the particle size decreases reaching a minimum of ~3 nm [05Ari]. Dai's group [09Gon] at Case Western University showed that gas-phase N-doping of CNTs would result in a metal-free electrocatalyst. After that, many studies revealed promising performance of N-doped carbon nanomaterials such as SWNTs [12Zha], graphene [10Qu], mesoporous graphitic array [10Liu], and carbon quantum dots [11Li] for replacing Pt-based catalysts [09Gon, 11Wan, 12Che]. Findings in Fe (or Co)/N/C systems and N-doped carbon nanomaterials may be combined possibly through using CNTs or graphene as support in Fe (or Co)/N/C catalysts instead of carbon black. However, it seems that carbon nanomaterials would have much more contribution in the next generation catalyst in fuel cells than what they have in current Pt/C commercial catalysts. Rational design of nanostructure of the so-called upcoming catalyst would be the key issue.

7.5.10 Self-Healing Li-ion Battery for Electric Cars

A "stretchy" polymer developed by scientists at Stanford University and the US Department of Energy's SLAC National Accelerator Laboratory in Menlo Park, CA, could open a path to self-healing electrodes in the lithium-ion batteries of future electric vehicles. The polymer coats a silicon electrode, binds it together, and

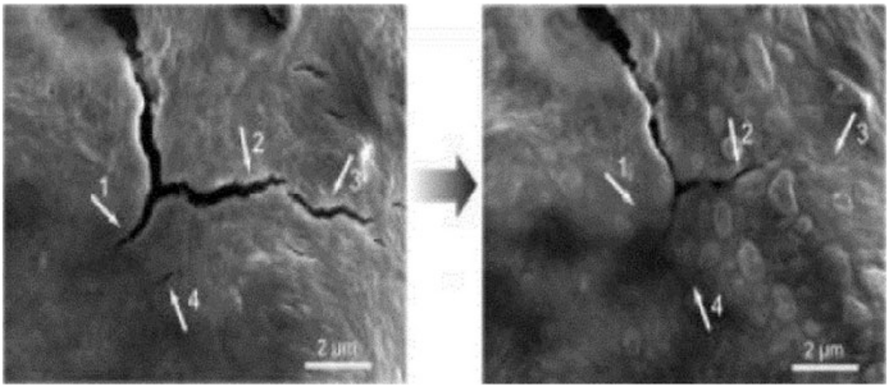


Fig. 7.22 *Left*: an electron micrograph shows cracks left in a self-healing polymer coating due to swelling of its silicon electrode during charging. *Right*: 5 h later, the smaller cracks have healed

spontaneously heals small cracks that develop during battery operation, the researchers said (as shown in Fig. 7.22). Carbon nanoparticles are added to the polymer to conduct electricity. Silicon electrodes swell to three times their normal size when ions flow into them during charging, then return to normal size upon release of the ions in discharge. Tests found that the electrodes lasted ten times longer when coated with the polymer, "which repaired any cracks within just a few hours," said Stanford Professor Zhenan Bao. A major challenge is to overcome the polymer's durability. Significant energy storage capacity loss occurred after about 100 charge–discharge cycles – far fewer than 3000 typical of an electric vehicle, the researchers acknowledge. "But the promise is there," said Yi Cui, an Associate Professor at SLAC and Stanford who led the research with Bao [13Cha].

To make the self-healing coating, scientists deliberately weakened some of the chemical bonds within polymers long chain-like molecules with many identical units. The resulting material breaks easily, but the broken ends are chemically drawn to each other and quickly link up again, mimicking the process that allows biological molecules such as DNA to assemble, rearrange, and break down. Researchers in Cui's lab and elsewhere have tested a number of ways to keep silicon electrodes intact and improve their performance. Some are being explored for commercial uses, but many involve exotic materials and fabrication techniques that are challenging to scale up for production.

The self-healing electrode, which is made from silicon microparticles that are widely used in the semiconductor and solar cell industry, is the first solution that seems to offer a practical road forward, Cui said [13Cha]. The researchers said they think this approach could work for other electrode materials as well, and they will continue to refine the technique to improve the silicon electrode's performance and longevity [13Cha].

7.6 Key Challenges for Polymeric Nanocomposites for Faster Commercialization

- Develop low-cost and high-production volume to meet fast to market needs.
- Develop fast, low-cost analytical methods with small quantity of samples which can provide a degree of exfoliation and degree of orientation, TEM, XRD, and rheology considered to be too expensive and time-consuming, for example, IR can detect silicon–oxygen bond in clay, which can help to evaluate degree of clay dispersion.
- Develop online testing of nanocomposites.
- Develop alternative nanoclay treatments for better adhesion of nanofiller to polymer.
- Improve understanding of the effect on performance by blending nanofillers with conventional reinforcements such as glass fiber.
- Prediction of orientation/flow modeling.
- Understand the rheology and chemo-rheology of the polymer composites.
- Cost/performance ratio to substitute high-impact polystyrene (HIPS), polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS), and polycarbonate (PC) with thermoplastics polyolefins (TPO).
- Fine dispersion, full exfoliation, and interfacial adhesion.
- High stiffness without affecting impact properties.

7.7 Opportunities and Future Trends for Polymeric Nanocomposites

The nanofillers are expensive compared to conventional fillers, so one must use them wisely depending on the final performance requirements of the parts. In many cases, it may be cost-effective to use nanofiller where it is needed such as on the top layer of a part surface or middle layer of thickness or localized areas of the part (nanocomposite premolded inserts). The advantages of nanotechnology applications are being demonstrated by R&D engineers, but commercial officers refuse to accept at increased costs. The nanoclays cost about $7/Kg and are used in loadings of 3–4%. The conventional competitor material is talc, which costs 65 cents/Kg and is used at loadings of 10–15%. Another issue of using nanofillers is that conventional tools may not give parts of desired dimensions. It requires extensive retooling because of the difference in shrinkage rate.

The use of nanopolypropylene (PP) for value-added substitution such as high-cost engineering plastics or development of molded-in-color nanocomposites to replace glass-filled, painted PP for interior applications such as instrument panels will see major growth. Functional nanocomposite development is underway such as functionalized clays which add properties to clay including antistatic and moisture-repellent characteristics and selective chemical barriers.

Ultraviolet-curable nanocomposites (electronics) and foaming and nucleating effect of nanofillers (improve properties, desirable cell size and density, use of microcellular processes such as MuCell) will be commercialized soon. There is potential for body panels and large moldings to substitute steel, aluminum, magnesium, and sheet-molding compound (SMC), where thermoplastics are currently not used due to inadequate physical or mechanical performance.

There is a need to develop low-cost carbon nanotube-based polymeric composites for high-end engineered plastics. For designing such composites, it is essential to develop flow simulation software with or without a hybrid fiber-filled system (including orientation effect and war page) so that the output of the simulation study can be used directly for structural analysis.

There are also many opportunities for development of new nanofillers and improvements such as nanocomposites of a new nano-ceramic fiber, titanium dioxide (TiO_2), magnetic particles, carbon nanotubes, carbon nanofiber, and other molecularly reinforced polymers. Mixtures of different nanomaterials or combinations of nanomaterials with traditional additives are increasingly being considered for carrying out innovative research.

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Polymer Nanocomposites for Adhesive, Coating, and Paint Applications

8

Sujata Pramanik and Niranjan Karak

8.1 Introduction

The saga of the utility of polymeric nanocomposites continues to expand across the domains from general purpose to special applications [03Fis, 03Hua, 04Ahm, 08Pau, 10Jan]. The use of polymers for adhesive, coating, and paint applications has received intense scrutiny since the last century, although its history dates thousands of years back [70Zan, 99Ger, 09Cho]. The tribute of the same goes to primitive men – the hunters and the cave dwellers – who decorated their objects and cave walls using varied natural colors. The limitations of poor physico-mechanical property, adhesive strength, wear and corrosion or chemical resistances, flame retardancy, and so on are addressed by the innovative approach of nanotechnology [03Sah, 05Szl, 07Hon, 09Soz]. However the use of nanomaterials in these domains is still in their infancy and particularly limited to special-purpose applications [09Hus, 11San]. The trio terms – adhesives, coatings, and paints – although exhibit the adhesion phenomenon but are different in many aspects including adherence of paints and coatings to one surface, while adhesive is sandwiched between two surfaces [05Ada]. The former possesses resistance to heat, moisture, or abrasion, while the latter inherent high bond strength to fracture apart the two substrates. However, adhesion is a key property of coatings and paints because the coating must adhere onto the surface to be decorated or protected [05Ada]. The polymeric matrices like epoxy [13De1], cyanoacrylate [96Gre], polychloroprene [00Pat], polyester [85Fun], polyurethane [85Sch], and vinyl ether polymers [92Ste] have established their supremacy in the arena of adhesive, coating, and paint materials.

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However the depleting petro-based resources are stimulating renewed interests in the use of bio-renewables in the domain of adhesives, coatings, and paints [00Kaw, 09Mei, 10Xia, 10Bha, 12Loc, 12Kar, 13Lli]. In other words, the conversion of these bio-based resources into polymeric matrices and exploration by different strategies to develop their nanocomposites endow green credentials, particularly in the times of the foreseen crisis of fossil fuels [00Kaw, 09Mei, 10Xia, 10Bha, 12Loc, 12Kar, 13Lli]. This approach of using the bio-resources will contribute toward sustainability in terms of following greener principles and partial substitution of the petro-based feedstocks [10Ana, 11Kum]. To cite for evidence is the development of adhesives, paints, and coatings using soy protein polymers [95Kal, 98Rhi], genetically engineered plant oils [04Wil], and so on. The soy proteins are amino acid polymers procured from by-products of processing oils which are chemically modified by different methods like acetylation, alkylation, hydrolysis, succinylation, and so on to tune in their gel-forming ability for the development of the adhesives and paints [07Mei]. On the other hand, the plant oils are triglycerides having three-arm star molecular structure with varied arm length (alkyl chain length), degree of unsaturation, and distribution of fatty acid contents [00Sri, 04Ere, 04Don, 08Çay, 09Rin]. In the exploitation of the active sites of the oils like unsaturation, allylic C-atoms, and carbonyl ester groups for attaching functional groups capable of polymerizing by polycondensation, ring-opening reactions help modulate the cross-linking density of the polymers for use as adhesives and resins in paint and coating industries [09Rin, 12Pra]. Apart from the above, plant starch [88Jon] and lignin [85You] also find potential uses in the aforementioned domains. Further the biodegradation of the same addresses the limitations of the known polymer waste management techniques like mechanical recycling and incineration [95Hua].

Further the achievement of advanced materials in the aforementioned realms calls either for modification of the polymers or formation of composite systems [09Kar]. The exudation of the modifier out of the polymeric matrix or the macrophase separation in the modification process forwards the preparation of nanocomposites wherein desirable property enhancement is achieved upon incorporation of small amount of appropriate nanomaterials [06Aja]. The inclusion of nanomaterials in a polymeric matrix changes the viscoelastic property of the pristine polymer whereby a higher energy is required for nanoscale mechanical deformation, consequently resulting in higher adhesive strength [03Mac, 04Kha]. Thus the soft polymeric chains armored with reinforcing nanomaterials including nanoplatelets and C-based nanomaterials are envisaged to possess potent adhesive property. The pronounced physico-mechanical, flame-retardancy and anticorrosive, and many other special properties of these nanocomposites forward them for use in paints and coatings [08Yeh, 09Das, 13Pra1, 14Pra1]. The exploration of the unique features like optical and electrical properties of nanostructured C-materials like carbon dots in the domain of paints and coatings is restricted to special applications only [13De2]. The advancement of the adhesive, paints, and coatings is summarized in Fig. 8.1.

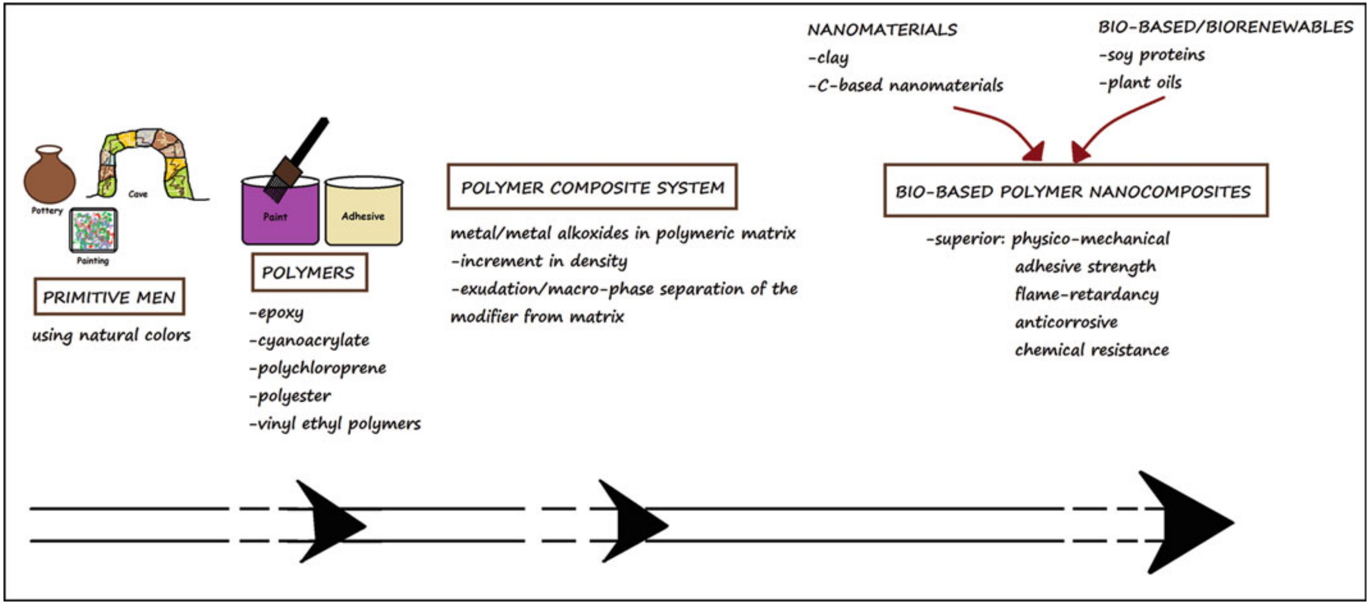

Fig. 8.1 Advancement of adhesive, paints, and coatings

Thus the trends in research innovations of the past decade and prospective of the nanocomposites of polymers with clay- and C-based nanomaterial are briefly discussed in the subsequent sections together with their structure–property relationships.

8.2 Modulations in Structure–Property

The presence of rigid linkages like cyclic structure or aromatic rings results in polymer with high T_g, essential for load-bearing structural adhesive applications [09Kar, 09Mai]. The use of polymeric nanocomposites as adhesives, coatings, and paints has to be compounded and made to undergo fabrication process prior to be converted into marketable products. The presence of polar functional groups renders pronounced wettability of the substrates and hence adhesion [09Awa]. Molecular weight of the polymers is also of concern owing to the requirement of good flowability and formation of rapid cure set [85Pep]. In this vein, the hyperbranched polymers prove to be an appropriate proposition owing to ease of diffusibility and desirable curing due to the presence of multitude of end-group functionalities and favorable architectural features [11You]. Clay forms one of the ideal nanomaterials for inclusion into a polymeric matrix among all other nano-reinforcements owing to their unique intercalation chemistry [00Ale, 03Ray]. The different modifying agents of clay lower the surface energy and improve the wettability of the inorganic nanoplatelets with the surrounding polymeric chains. The variations in the chain length and nature of functional groups of the clay-modifying agent dictate its interfacial interaction with the polymer and hence modulate the properties of the nanocomposites accordingly. In other words, the impregnation of different modifying agents in the clay galleries influences the surface properties of the clay nanocomposites to be used in paints and coatings, which determine the resistance of the same toward environmental factors like corrosive chemicals, weather, moisture, and so on [09Kon, 14Pra2]. While the clay exists as two-dimensional nanoplatelet geometry, C-based nanomaterials exist in all the three forms, viz., zero-dimensional carbon dots, one-dimensional carbon nanotubes, and two-dimensional graphene platelets. In parallel lines with the clay, functionalization strategies of C-based nanomaterials also merit in support of the modulation of the properties by grafting on desired functional moieties onto their backbone or sheet surface [06Guo, 07Hay, 07Wan1, 09Yan, 13Pra2]. The pronounced stress transfer between the polymer and the nanomaterials increases the yield point or breaking stress, consequently resulting in superior adhesive property over the pristine polymer [04Wag]. These nanocomposites are the materials of choice as adhesives over the mechanical fastening joints in terms of smooth distribution of stress in the former as compared to localized stress concentration in the latter [04Dun]. These nanomaterials in the polymeric nanocomposites exhibit high reinforcing efficiency which influences the hardness and physico-mechanical and thermal properties of the pristine polymer for utility in coating applications [08Yeh, 13Pra1, 14Pra1]. The physico-mechanical performance of the paints is of foremost importance in context of protection when subjected to varied mechanical stress and deformations or strains during their active service lifetime. The advantages of long-term abrasion and scratch resistances of these nanocomposites over the pristine polymeric system find use in surface protection or coating applications across the domains from textiles to electronics to consumer products [08Kow]. Significant improvement in the barrier properties and retention of the transparency of the coatings make these nanomaterials ideal candidate for inclusion in the polymeric matrices [07Ebi]. The increasing content of the nanomaterials influences the T_g of the polymeric nanocomposites, which in turn decrease the sliding coefficient of friction of the latter, consequently enhancing their wear resistance [09Kar, 09Mai].

The subsequent subsection discusses the role of clay- and C-based nanomaterials in governing the adhesive and coating properties of the nanocomposites.

8.2.1 Clay-Based Polymeric Nanocomposites

The adhesive property of polymeric nanocomposite is directly dependent on two factors, viz., the presence of polar functional groups and physical interlocking of the nanocomposite with the adherent [13De1]. These polar functional moieties of the nanocomposite subsequently generate strong interactions with the polar substrates like cellulose present in the wood substrate and wet the two substrates thereby result in close contact between the two across the interfaces [09Kar]. The diffusibility of the nanocomposites and formation of van der Waals interactions to hold the substrates together, sandwiching the nanocomposite, also count in the formation of physically interlocked structure with the substrate [06Aja, 09Kar]. The presence of nanomaterials renders high interfacial interactions (aids in cross-linking density in case of thermosetting polymers) with the polymeric matrix and is thus instrumental in increasing the tack adhesion strength [11Das]. In other words, higher amount of energy is required for debonding the adhesive relative to that in case of pristine polymer. The incorporation of nanomaterials induces an increased elastic behavior (storage modulus) and, consequently, lowers the resistance to creep under shear stress as compared to the pristine polymer [10Dil1]. The transition from liquid-like viscous behavior in polymer to solid-like elastic behavior in the nanocomposites results in higher energy required for deformation, and hence higher adhesion energy. To this end, Wang et al. documented an increase in the tack adhesion energy of clay-based poly(butyl acrylate-co-acrylic acid) nanocomposite by 70 % as compared to PBA latex [09Wan]. An important structure–property correlation upon the incorporation of clay into polyester-based polyurethane nanocomposites with emphasis on their physico-mechanical and adhesion property was put forward by Maji et al. [09Maj]. De et al. has reported twofold amount of perk in the adhesive strength of poly(amidoamine)-modified clay-based hyperbranched epoxy nanocomposites as compared to the pristine hyperbranched epoxy using both wood and metallic substrates [14De]. The study highlighted the role of interactions of O- and N-containing functional groups in clay-based hyperbranched epoxy with the substrate to result in enhanced adhesive strength [14De]. The use of bio-based polymeric nanocomposites seems promising in regard to nonstructural or pressure-sensitive adhesives owing to the presence of long aliphatic fatty acid chains which impart sufficient flexibility and T_g. In this milieu, Deka et al. focused on the use of bio-based hyperbranched polyurethane/clay nanocomposites for adhesive applications [11Dek]. Moreover, the works of Karak and his coworkers highlighted the influential role of a multitude of end-group functionalities present in the hyperbranched architecture of the nanocomposites [11Dek, 14De]. The presence of a large number of peripheral functional groups in the hyperbranched polymers resulted in higher interfacial interactions including secondary interactions like H-bonding, electrostatic, polar–polar, and so on to result in enhanced adhesive strength over that of their linear analogs [11Dek, 14De]. This fact is also supported by the study of adhesive property of hyperbranched poly(amino ester) by Zhang et al. [14Zha]. Further the inclusion of clay increased the number of such interactions of the polyurethane-clay nanocomposites with the adherent substrate, which was evident from the observation of their dose-dependent increment of adhesive strength by Rahman et al. [07Rah].

Moreover, the clay is bequeathed with trunk load of properties including physico-mechanical, thermal, and chemical which have fetched the clay nanocomposites a colossal share in the realm of paints and coatings [09Kar]. The study of Sun and his coworkers attested improvement in the moisture barrier and coating properties of the clay-based waterborne polymer nanocomposites over the pristine polymeric latex [07Sun]. The vegetable oil-based highly branched polyester–clay nanocomposites showed superior performance relative to that of the pristine polyester for use as advanced coating materials [09Kon]. These nanocomposites containing 5 wt% clay exhibited three times increment in the tensile strength, four times increment in the elongation at break, and 18 °C enhancement of thermostability. This report by Konwar et al. attested the amalgamation of the highly branched architecture and clay in influencing the properties of the nanocomposites [09Kon]. Spurred by the above findings, Das et al. exploited the thermostability of the clay nanoplatelets and investigated the flame retardancy of the *Mesua ferrea* L. seed oil-based epoxy/clay nanocomposites [09Das]. The rate of heat release and loss of mass diminished upon thermal degradation of clay nanocomposites as compared to that of the pristine polymeric matrix, consequently endowing higher flame retardancy to the former [09Das]. Further the findings of Deka et al. were in parallel lines with the above antecedents [10Dek]. Deka et al. prepared *Mesua ferrea* L. seed oil polyurethane-s-triazine ring containing poly(amidoamine)-modified clay nanocomposites [10Dek]. The noticeable credits of this study included dramatic improvements in the tensile strength (1.7 times), thermostability (131 °C), scratch resistance (2.3 times), and flame retardancy without compromising the effect on other properties like elongation at break or impact resistance as compared to the neat polymer [10Dek]. Pramanik et al. documented nanocomposites of polyaniline nanofibers modified clay and castor oil-based hyperbranched poly(ester amide) for use as antimicrobial coating materials [14Pra2]. These thermosetting nanocomposites with pronounced physicochemical, thermal, and mechanical properties exhibited a wide spectrum of antimicrobial activity against bacterial and fungal strains and algal consortium [14Pra2]. The key role of nanoscaled polyaniline is highlighted in context to the antimicrobial efficacy of these nanocomposites [14Pra2]. The abovementioned reports highlight the role of modifying agent in influencing the properties and performance of the pristine polymer [09Das, 09Kon, 10Dek, 14Pra2]. The field of clay-based hyperbranched polymeric nanocomposites thereafter gained momentum, and the lion's share of the same found utility in coating industries.

8.2.2 Nanostructured C-Based Polymeric Nanocomposites

Although the unique features like high electrical, mechanical, thermal, physico-mechanical properties of C-based nanomaterials were hyped in various nanocomposites [06Guo, 07Hay, 09Yan, 13Pra2], but the research on the influence of the presence of the same nanomaterials in polymeric matrix on their adhesive property is scanty. The poor adhesive performance of pristine polymers and the need of flexible and optically transparent electrically conductive adhesives urge the use of C-based polymeric nanocomposites in this context. The single-walled carbon nanotube pressure-sensitive adhesives cater the need of conductive adhesives and are thus preferred over the adhesives based on ceramics like indium tin oxide to find uses in electronic display technologies. To cite for evidence, poly(butyl acrylate) single-walled carbon nanotube nanocomposites possess adequate elastic energy resulting in the maximum tack energy as compared to the pristine polymer [06Wan]. Moreover, the incorporation of single-walled carbon nanotubes in low concentration affords the nanocomposite adhesive film transparent [06Wan]. Among the few reported works, De et al. observed an increment in the adhesive strength of carbon dot-based hyperbranched epoxy nanocomposites [13De2]. This is attributed to the interfacial interactions between the polar functionalities present on the hyperbranched epoxy backbone and carbon dots [13De2]. The correlation between the storage modulus of the nanostructured carbon dot-based polymeric nanocomposites and increasing content of such C-based nanomaterials has not been studied till date, and thus it forms one of the prospective areas of research yet to be proved into.

The versatile and outstanding properties of C-based nanomaterials improve mechanical and resistance against corrosion of polymers, which forwards them as a potent candidate for top-layer coatings. Siddiqui et al. employed epoxy–carbon nanotube nanocomposite as "healing" coating onto the brittle glass fibers to dissipate the stress formed on the fibers apart from enhancing their reinforcing efficiency [09Sid]. This finding showed significant improvement in the tensile strength of the fibers upon impregnation of 0.3 wt% epoxy–carbon nanotube nanocomposite coating onto the fiber surface [09Sid]. Srinivasan et al. studied the unison of conducting polymer and carbon nanotubes in the domain of smart coating materials [08Sri]. They fabricated oligo(p-phenylenevinylene)–carbon nanotube nanocomposites via self-assembly approach for use as superhydrophobic coatings onto mica, metal, and glass surfaces [08Sri]. These coated materials possessing obtuse water contact angle (165–170°) and a sliding angle of >2° were employed as superhydrophobic self-cleaning surfaces [08Sri]. Karak and his group made significant contributions in this milieu [13Dek, 13Pra1, 14Pra1]. Vegetable oils

Table 8.1 Utility of polymer nanocomposites using clay- and C-based nanomaterials as adhesives, paints, and coatings

Clay–polymer nanocomposites	C-based nanomaterial–polymer nanocomposites
(A) Adhesives	
(i) Clay-based poly(butyl acrylate-co-acrylic acid) nanocomposites [09Wan]	(i) Poly(butyl acrylate)–single-walled carbon nanotube nanocomposites [06Wan]
(ii) Clay into polyester-based polyurethane nanocomposites [09Maj]	(ii) Carbon dot-based hyperbranched epoxy nanocomposites [13De2]
(iii) Poly(amidoamine)-modified clay-based hyperbranched epoxy nanocomposites [14De]	
(iv) Clay-based hyperbranched poly(amino ester) nanocomposites [14Zha]	
(v) Bio-based hyperbranched polyurethane-clay nanocomposites [11Dek]	
(B) Paints and coatings	
(i) Clay-based waterborne polymer latex nanocomposites [07Sun]	(i) Epoxy–carbon nanotube nanocomposite [09Sid]
(ii) *Mesua ferrea* L. seed oil-based highly branched polyester–clay nanocomposites [09Kon]	(ii) Oligo(p-phenylenevinylene)–carbon nanotube nanocomposites [08Sri]
(iii) *Mesua ferrea* L. seed oil-based epoxy-clay nanocomposites [09Das]	
(iv) *Mesua ferrea* L. seed oil polyurethane-s-triazine ring containing poly(amidoamine)-modified clay nanocomposites [10Dek]	
(v) Polyaniline nanofiber-modified clay and castor oil-based hyperbranched poly(ester amide) [14Pra2]	

ranging from dual-purpose sunflower oil to nonedible castor oil and *Mesua ferrea* L. seed oil were explored by this group for the synthesis of the different polymeric matrices for the formation of the nanocomposites. Although the group studied the coating performance of nanostructured C-based polymeric nanocomposites, the reports documented the utility of these nanocomposites for special purpose applications ranging from shape-memory to antistatic materials [13Dek, 13Pra1, 14Pra1]. Table 8.1 highlights the prominent research works on the use of polymer nanocomposites using clay- and C-based nanomaterials as adhesives, paints, and coatings.

The next section is focused on brief discussion on the types of polymer nanocomposites used as adhesives and coating materials.

8.3 Classification

The previous sections highlighted the impact of change in the structure onto the resultant properties of the material for use as adhesives, coatings, and paints. The polymeric nanocomposites as adhesives, coatings, and paints are classified on the basis of their physical properties or behavior.

8.3.1 Polymeric Nanocomposites as Adhesive

8.3.1.1 Structural

The structural adhesives are high-performance adhesives which are capable of resisting substantial load where strength, stiffness, and adherence properties for assembling two load-bearing engineering substrates are important [10Dil2]. The adequate density of primary interfacial bonding (i.e., covalent bonds) is necessary for the wettability of the two substrates and to afford high bond strength and durability. Apart from the above, these adhesives should possess significant tensile shear and peel strength, impact, and fluid resistance and withstanding ability to resist high and low temperatures [10Dil]. They are employed to strengthen, repair, or bridge the crack and subsequently arrest the crack propagation for use in the construction and building applications [10Dil]. These adhesives are hardened or cross-linked or polymerized in different ways, viz., using high temperature, radiation, or by drying of the solvent [03Dec]. The cross-linked thermoset polymers are favored over the thermoplastics for the same owing to relatively higher creep resistance at elevated temperature or moisture conditions [05Fis]. To this end, epoxy-based adhesives possessing relatively high strength and modulus are commonly used for fixing load-bearing joints [75Bas]. The significant performance, resistance to failure, and creep forward the thermosetting epoxies as adhesives for load-bearing engineering applications [75Bas]. The increase in glass transition temperature (T_g), toughness, and adhesive fracture energy upon incorporation of the nanomaterials play a significant role in the use of the nanocomposites as structural adhesives. The graphene oxide or reduced graphene oxide nanoplatelets exhibit comparatively greater reinforcement owing to the higher intrinsic stiffness than the clay [10Com]. The charge–transfer interactions between the silicate platelets of clay and cyanate ester resin result in high interfacial adhesion between the same for use of such nanocomposites for structural adhesives [03Gan].

8.3.1.2 Semi-structural and Nonstructural

The semi-structural and nonstructural adhesives are those adhesives which are employed for relatively low load-bearing applications where failure is less critical or for aesthetically important finished products [10Dil]. The design of polymer containing a combination of rigid and linear aliphatic chains in its backbone is sufficient for utility as semi-structural and nonstructural adhesives [10Dil]. Polyamide adhesives possess desirable strength and flexibility adequate for different applications [80Pee]. The blended cross-linked functionalized polyolefins with tackifiers for use as semi-structural adhesives for adhering the material of interest onto oily galvanized steel surfaces [95Tse]. The increment of adhesive bond strength of the blends over the respective materials was either low or marginal with the degree of interfacial bonding being correlated with the failure of the lap shear bonds [95Tse]. In this regard, the high surface energy and aspect ratio of the clay nanomaterials sounds promising in enhancing the degree of interfacial bonding and strength of their nanocomposites as compared to that of the reported polymer blends [11You]. Inspired from the above fact, Azizi et al. reported the silane-grafted-polyethylene–clay nanocomposites exhibited higher percent gel fraction relative to the pristine polyethylene [10Azi]. The cross-linking kinetics was found to increase with the increasing content of clay in the nanocomposites [90]. The physico-mechanical performance of these nanocomposites including tensile strength increased, while the elongation at break and melting point shifted to lower magnitude [10Azi]. The C-based nanomaterials have found utility in the arena of conductive adhesives utilized in lieu of conventional solder technology using tin–lead alloy in the electrical applications like liquid crystal display, flip-clip assembly, and so on. The concerns over the lead hazard have instigated the use of lead-free electrically conducting adhesives [06Li]. Irvin and his coworkers have patented the conducting adhesive formulation using multiwalled carbon nanotubes for use in semi- or nonstructural applications including laminates in device components [06Irv].

8.3.1.3 Pressure-Sensitive

These are soft and deformable low modulus self-adhesives which are designed to glue on substrates by simple contact mechanism under minimal amount of pressure [10Dil]. The heat-seal and laminating adhesives on the other hand require temperature in the form of activation energy [89Ura, 07Tra]. The presence of linear aliphatic polymeric chains with few polar functional groups exhibiting weak van der Waals forces is sufficient for maintaining the contact between the adherent substrate and the adhesive in these applications [07Tra, 09Kar]. The ease of handling marshals in support of the use of same for general purpose applications to decorative laminates [07Tra]. The tackifying resins and acrylics are generally used in this regard [07Tra]. They find uses in packaging, electrical mending, mounting, and masking [94]. The clay-based adhesive formulation exhibits significant improvement in the tack and shear resistance and peel strength as compared to the bare ones. To this end, the octylamine-modified clay-based polydimethylsilioxanes are used in pressure-sensitive adhesive-based controlled drug release technology for transdermal biomedical applications [00Lan]. Bonnefond et al. explored the miniemulsion polymerization technique for the preparation of (2-methacryloylethyl) hexadecyl dimethylammonium-modified clay-based polybutyl acrylate or polymethacrylate nanocomposites as waterborne adhesives [13Bon]. The study attested the role of modified clay over the unmodified one in imparting enhanced shear and peel resistances, shear adhesion failure temperature, and energy of adhesion to the nanocomposite films [13Bon]. This is attributed to the improvement in the wettability of the clay with or its encapsulation within the monomer droplets which promotes adhesion [13Bon]. A key observation by Wang et al. documented 85 % enhancement of the energy of adhesion of the pressure-sensitive adhesives upon 0.3 wt% loading of carbon nanotubes into the matrix together with marinating the optical transparency [09Wan].

8.3.2 Polymeric Nanocomposites in Coating and Paint

The paints are defined as the pigmented materials which form a thin continuous layer to the applied surface to serve the requirements of protection and aesthetic appearance [06Pat]. A typical architectural paint comprises of primer, undercoat, and topcoat. The prime requirements in surface coatings and paints are diverse, starting from protecting the surface from environment (decorative coatings), wear and tear or abrasion, high temperature, and moisture resistance (employed in electronics) to durability upon prolong contact with aqueous medium (marine enamels) [06Pat]. The inclusion of nanomaterials particularly clay into a polymeric matrix affords intumescent coating owing to their flame retardancy and mechanical robustness [09Das]. Among all others, alkyd resins still continue to form the workhorse of the coating and paint industries owing to their versatility to tune in their structure–property and cost-effectiveness [09Kar, 12Kar]. These resins impart many advantages including conferring green credentials when they are obtained from bio-renewables [08Kow, 12Kar, 13Pra3]. The presence of different fatty acid compositions of vegetable oils in the resin structure modulates the drying characteristics along with their other physico-mechanical properties [12Kar]. The urethane alkyds, epithet as uralkyds, are preferred choice in myriad of applications from wood finishes and metal primers to naval coatings and maintenance paints owing to their superior adhesion, strength, durability and abrasion, and chemical resistance than the unmodified alkyds [06Pat, 12Kar]. The high-solid alkyd resins find uses in industrial baking finishes. The clay acts as a rheological modifier more particularly as a thixotropic agent in the application of polymeric clay nanocomposites for coatings and paints [09Kar]. They greatly enhance the rheological properties of the paint system. They prevent pigment settling and sagging on vertical surfaces, and gloss is minimally affected due to lower level of addition [99Lam]. Color is a property, and gloss is the attribute accountable for the lustrous appearance of the paint system [99Lam]. The fluorescence property of C-dots instigates its use for special paint applications [13De2]. The clay- and C-based nanomaterials are instrumental in imparting high heat-distortion temperature and flame-retardancy properties in addition to significant mechanical, electrical, and magnetic properties to result in high-strength polymer nanocomposites for applications across the domains as special-purpose coating materials [08Yeh, 09Das, 13Pra1, 13De2, 14Pra1]. The drive toward the use of oleoresins vanishes, although it has a comparatively lower drying rate than the synthetic ones which can be overcome by the nanotechnology, and addresses the sustainability constraints [09Kar].

8.3.2.1 Solvent-Borne and Waterborne

The solvent-borne coatings are primarily employed in heavy wear and tear areas like kitchen, bathroom, and so on where resistance toward oil, grease, etc. is required [99Lam, 06Pat]. The concerns over the issues of solvent vapor emission of the solvent-borne paints instigate the use of high-solid and waterborne coatings which reduces the volatile organic content (VOC) and imparts comparatively better safety against fire and health hazards of the toxic solvents [99Lam, 06Pat]. Further, the continuation of oxidation post cross-linking or chances of microcracking of the film upon overbaking deteriorate the film together with loss of gloss [99Lam]. These water-based paints on the other hand enjoy a number of advantages over the solvent-based ones including low odor, fast drying and recoating, and ease of cleaning

[99Lam, 06Pat]. The waterborne resins are prepared by different strategies, viz., alkyd resins are converted into an emulsion state, water-soluble functional moieties like carboxyl groups are incorporated or formation of ionic structure in the backbone of the resin, etc. [99Lam, 06Pat]. These paints are generally of two grades, viz., high quality based on acrylic paints and cheap quality based on copolymers of acrylic/vinyl acetate or styrene [99Lam]. The acrylic paints exhibit excellent durability, good wet adhesion, and color and gloss retention as compared to the copolymeric paints. However, low T_g of the pure acrylic paints forms the bottleneck in their practical applications by limiting their service temperature [99Lam]. The requirement of low viscosity in high-solid paints highlights the use of hyperbranched or dendritic polymers in this regard [09Kar, 12Kar]. The modulation of the clay surface using varied intercalants dictates its hydrophobicity-to-hydrophilicity ratio which plays decisive role in the use of its nanocomposites either for solvent-borne or waterborne paints [14Pra2]. The intercalation of salts of polyacrylic acid and polymethacrylic acid, polyethylene glycol, quaternary ammonium salts, poly(vinyl oxazolidinone) and its copolymers, and so on into the clay galleries teaches us the use of its nanocomposites as waterborne paints [99Lam]. The use of long fatty acid containing vegetable oils as the starting material for the synthesis of the polymeric substrates forwards the use of its nanocomposites as organic solvent-borne paints [12Kar].

8.3.2.2 Bioerodible and Peelable Medical

The bioerodible coatings are employed for internally used biodegradable substrates or prosthetic devices in biomedical domains [12Kar]. The corrosion resistance property of the metal alloys forwards their uses in fabrication of prosthetic devices. However the biocompatibility of these alloys with different body tissues/organs and blood cells poses the major hurdle in their practical utility [76Bok]. In this vein, literature reports the employment of adherent, biocompatible, and thromboresistant pyrolytic carbon coatings onto prosthetic devices which exhibit pronounced compatibility with the blood or tissues [76Bok].

The peelable coatings, on the other hand, are nontoxic coatings with desirable hot tack, adhesion to a variety of substrates, and controllable peel strength and find utility in biomedical domain [99Lam]. They must be sterilizable and should possess porosity so as to prevent pressure buildup during gas sterilization process [99Lam]. They are employed for packaging films for sterilized articles like dressings, surgical instruments, and so on [99Lam]. The package and its contents are subjected to autoclaving temperature thereafter to render the whole material sterilized [99Lam]. The clay- and C-based nanomaterials may be effective in modulating the barrier property of the polymeric nanocomposites used in this regard. The use of bio-based resources like vegetable oils possessing long fatty acid chains exhibits plasticization effect and influences the peel strength of the coating material, apart from contributing toward sustainability [12Kar].

8.3.2.3 High Performance

Both thermosetting and thermoplastic polymers with at least one special attribute are used for this purpose. The thermoset coatings constitute a key section of the aerospace interior furnishings [99Lam]. These forms a three-dimensional cross-linked network structure on curing with different curing agents, and the incorporation of nanomaterials in these polymeric matrices aids in the curing reaction [09Kar]. Epoxy resins are highly priced among others such as thermosetting resins owing to their strength, creep resistance, corrosion and weather resistance, high heat deflection temperature, and so on [05Rat]. The hydroxyl-terminated or hydroxyl-substituted quaternary ammonium functional moieties of the clay and varied functional groups engulfed onto the surface of C-based nanomaterials afford perk in the intragallery cross-linking reaction of such thermosetting resins [00Ale, 03Ray, 13Pra1, 14Pra1]. Literature reports that such exfoliated clay–polymer nanocomposites possess adequate flexibility contributing to the good coating properties of the nanocomposites [00Ale, 03Ray, 09Kon, 14Pra2].

Hou et al. documented the role of such thermoplastic nanocomposites in the domain of paints and coatings [08Hou]. The pronounced mechanical strength, wear resistance, and so on of the polyetheretherketone–fullerene nanocomposites are forwarded for use as high-performance coatings for special applications [08Hou]. Steurer and his coworkers investigated the role of zero-, one-, and two-dimensional C-based nanomaterials in enhancing the property profile of the thermoplastics like polyamides and polycarbonates [09Ste]. The report showed that the exfoliated graphene oxide platelets were superior as compared to zero-dimensional fullerene or carbon black and one-dimensional carbon nanotubes in this perspective [09Ste]. The improvement in the electrical and thermal conductivities, infrared absorption, heat distortion temperature, electromagnetic shielding, nonflammability, antistatic property, and so on forwarded these graphene oxide-based thermoplastic nanocomposites for use in special-purpose coatings [09Ste].

8.3.2.4 Sol–Gel

Sol–gel-derived coatings are employed for the chemical and oxidation stability and protection against erosion wear and corrosion of metallic substrates [99Lam, 05Mah]. The sol–gel films are deposited onto the metals to modify their surface attributes and render their resistance toward oxidation and wet corrosion. The deposition of these sol–gel coatings is well suited for the side coating of the optical fibers and waveguides of evanescent-wave sensors owing to the precise control of their sensitivity-determining parameters including film thickness [99Lam]. This method is based on the principle that ceramics are comparatively more resistant than the metals [99Lam]. In this vein, the use of polymeric nanocomposites of clay- and C-based nanomaterials has a special merit as coating materials. The combination of properties typical for ceramic such as hardness, scratch, and abrasion resistance which impart superior wear resistance along with their many other physico-mechanical, optical, electrical, and biological properties, oleophobicity, viscoelasticity, and so on of the polymeric matrices affords special edge to the polymeric nanocomposite-based sol–gel coatings [09Wan]. This method of surface protection is an environmentally friendly technique which holds potential for the substitution of traditionally used toxic pretreatments or coatings in this milieu [09Wan]. Ahmad et al. incorporated reinforcing ceramics into the high-performance host polyimide matrix [01Ahm]. Avnir further reviewed the chemistry of the unison of polymers and ceramics as doped sol–gel materials [95Avn]. Soucek and Wold patented a bio-based ceramic coating formulation employing polycondensation of metal alkoxides in polymeric matrices via in situ sol–gel process for use as corrosion-resistant coatings on metallic substrates [00Sou]. The drying/semidrying vegetable oils like linseed oil, dehydrated castor oil, tung oil, perilla oil, soybean oil, and so on and their mixtures were used as the binder in the paint formulation reinforced with ceramics like titanium and zirconium sol–gel precursors for accelerating the drying process [00Sou].

8.3.2.5 Radiation-Cured

The radiation-cured coatings are a cost-effective substitute to the traditionally used less eco-friendly two-pack polymeric systems [99Lam]. These coatings contain photoinitiators which are radiation-activated using mercury vapor/electrodeless vapor/pulsed xenon/laser lamps to generate active free radical species, which interact with unsaturation in the monomer/resin to subsequently polymerize to result in a solid cured film [99Lam]. The photoinitiators having strong absorption at the emission line of the high-energy radiations used undergo photolysis to either produce active radicals used to cure acrylate monomers or generate cationic species to cure cycloaliphatic epoxy-based systems [07Lee]. In this regard, it is pertinent to mention the ultraviolet absorption by the clay (upon modification using microwave-absorbing functional groups) and microwave absorption by the C-based nanomaterials which hold promising avenue in context to the radiation-cured coatings. Lee and Kim reported the ultraviolet curing of the urethane acrylate-based clay nanocomposites [07Lee]. The nanocomposites exhibited dose-dependent increment in the physico-mechanical, thermal, and optical properties [07Lee]. Rangari et al. documented the curing of the epoxy–carbon nanotube nanocomposites (low loading of 0.1–0.3 wt% carbon nanotubes) upon exposure of 2.45 GHz microwave radiation [10Ran].

8.3.2.6 Antimicrobial

The scientific findings in the present decade document C-based nanomaterials armored with polymeric matrices as potent antimicrobial coating materials [08Nep]. The modification of the surface hydroxyl groups or exchange of intergallery cations of the clay with antimicrobial functional moieties offers a promising solution in context to the cutting-edge quest for low-cost antimicrobial coatings [00Ale, 03Ray, 06Pat]. These coatings find a number of applications ranging from medical devices including surgical implant surfaces to packaging and textiles [14Pra2]. An easy and inexpensive antimicrobial coating material to provide long-term protection against microorganisms with enhanced antimicrobial efficacy is the need of hour. In this context, the inclusion of minimal amount of the afore-stated nanomaterials with desirable antimicrobial efficiency will suffice our need to anticipate future challenges. Poly(vinyl methyl ether)s are used as antifouling paints [01Cod]. Pramanik et al. combined the antimicrobial attributes of polyaniline nanofiber-modified clay and bio-based hyperbranched poly(ester amide) for fabricating antimicrobial coating material [14Pra2]. Another recent report by the same group documented the inclusion of comparatively lower content of multiwalled carbon nanotubes into the bio-based polymeric matrix than the earlier report [14Pra2] for conferring antimicrobial attributes to the nanocomposites [14Pra3].

8.4 Application

After an introductory section to the structure–property relationships and types of polymeric nanocomposites of clay- and C-based nanomaterials, a thorough overview of the diverse applications of the same is discussed underneath. The focus on the research of adhesives, coatings, and paints is being steadily shifted from polymeric matrices to the development of nanocomposites for the design of novel drug delivery to automobile applications.

8.4.1 Adhesive

8.4.1.1 Biomedical

The use of adhesives in biomedical domain engulfs a number of materials including adhesive dressing, osteomy bag mounts, surgical drapes, and so on [76Kro, 98Hoo]. The prime requirements for an adhesive bandage and epithet as “perfect surgical glue” which are mimicry of the mechanical strength as the healthy tissue, that is, tissue adherence strength, must be tacky and not elicit any toxic inflammation to the surrounding undamaged tissues and should degrade with minimal scarring [76Kro]. Alkyl cyanoacrylates are largely used as surgical tissue adhesives in biomedical and healthcare domain such as embolization treatment of brain arterio-venous malformation, repair of retinal detachment, and so on [90Tor]. The pressure-sensitive adhesives help adhere dressing bandages to a wound [89Ura]. The mixture of gelatin and resorcinol cross-linked with formaldehyde finds use as adhesive bandages for aortic dissection repairs and hepatic and renal tissues [12Dua]. The fibrin glue, available under the trade names of Tissucol, Beriplast and Biocol, is used as biological adhesives during heart bypass, colon or traumatic spleen surgeries to seal in the blood vessels, and as controlled release agents for drugs [01Cur]. Polyurethane with adequate moisture permeability is used as adhesive dressings allowing moist wound healing [96Bog]. The conventional polymers used in the biomedical applications suffer from the problem of undesired dehydration process. The afore-stated drawback of the same is addressed by forming nanocomposites. The inclusion of nanomaterials into the polymeric matrices increases the cross-linking density and percent gel fraction, which consequently decreases the rate kinetics of removal of water and prolonged their dehydration process [07Lee]. Further the degradability of the adhesive dressings in the presence of body fluid is an important aspect in case of burn wounds, wherein the use of vegetable oil-based polymers seems to be promising. The effectiveness of these tissue adhesives is also influenced by internal sealant bonding strength, tissue healing, and infection controllability [07Lee]. Thus the antibacterial activity of the adhesive bandages is another key concern owing to the invasion of wound by different microorganisms [03Mer]. In this vein, the antimicrobial activity of the C-based nanomaterials merits a special mention. Pramanik et al. have reported the use of functionalized multiwalled carbon nanotubes into bio-based hyperbranched poly(ester amide) imparts antibacterial efficacy along with other desirable attributes of a dressing material [14Pra3]. The nanocomposite films with multidrug-resistant bacteria antibacterial attributes, biocompatibility with peripheral blood mononuclear cells, and biodegradability in simulated body fluid forwarded the nanocomposite films for use as dressing material for infected burn wounds [14Pra3]. Further, the metal oxide–multiwalled carbon nanotube nanohybrids are also exploited in the domain of biomedical and healthcare applications. In this regard, Das et al. fabricated sunflower oil-based hyperbranched polyurethane nanocomposite using iron oxide nanoparticle-decorated multiwalled carbon nanotubes for use as an efficient wound dressing material with controlled drug release property [14Das]. The multifaceted nanocomposite possessed antibacterial activity, biocompatibility, hemocompatibility, and nonimmunogenic property [14Das]. Further, the nanocomposite dressing patch exhibited significant fluid handling capacity, wound healing potency, moisture vapor permeability, and controlled gentamicin sulfate loading and release efficacy for more than 72 h [14Das]. These findings on the use of functionalized nanotubes aptitude for antibacterial wound healing material [14Das, 14Pra3]. However, the rigorous safety appraisal limits the use of nanotechnology in this regard.

Mucoadhesives merit a special mention in context to the bio-adhesives which are designed to glue mucosal surface with the drugs for pronounced therapeutic outcome [96Pep]. These mucoadhesive dosages enable the controlled release of the drugs and patient compliance and benefit over the short residence time of the oral route and for the drug molecules which are prone to acid or enzymatic degradation [96Pep]. These drugs are formulated as powders, sprays, viscous liquids, and films, and the various polymers used in this regard are cellulose and chitosan derivatives, polyethylene glycol, hydrogel, poly(acrylic acid) available under the trade name of Carbopol®, poly(methyl vinyl ether)–maleic anhydride copolymer commercialized under the brand name of Gantrez®, and so on [96Pep]. Lee et al. provided light on the use of clay-based polymeric nanocomposites as mucoadhesives [04Lee]. These researchers investigated the effect of the clay on the mucoadhesive property of a series of hydrogels and xerogels [04Lee]. These three-dimensional networks of homo- or copolymeric gels are prepared by photopolymerization technique using monomers like acrylic acid, methyl ether acrylate, ethylene glycol, and so on [04Lee]. The incorporation of clay in these polymeric gels reinforced their structure to afford superior physico-mechanical, chemical, and biological properties as compared to the pristine gels [04Lee]. The various functional groups adhered onto the surface of the nanomaterials permit the increased intermolecular interactions of the nanocomposites with the desired substrate to favor superior mucosal adhesive property, as supported by different theories of bio-adhesion, viz., wetting, electrostatic, and adsorption theories [04Lee]. The clay attracts attention amid other nanomaterials owing to their unique mechanical properties and excellent porosity, hydrophilicity, and biocompatibility in biomedical applications [00Ale, 03Ray]. The study attested the significant release behavior of drug cargo loaded onto these nanocomposites as compared to the pristine gel polymers [04Lee]. Further the inherent antimicrobial activity of the C-based nanomaterials has significant role in retarding pathogenicity, one of the major problems confronted for utility of the mucoadhesives [11Sha]. A recent report by Moridi et al. highlights the preparation and property evaluation of carbon nanotube-chitosan nanocomposites [11Mor]. However this technological advancement awaits for the inclusion of carbon nanotube polymeric nanocomposites in the arena of mucosal drug delivery system.

The poly(methyl methacrylate)-grafted clay nanocomposites prepared by the free radical polymerization method in the presence of surfactant-modified clay as the reactive component find use as dental adhesives [09Ata]. The good dispersion stability of the nanoplatelets of the modified clay in the nanocomposites was instrumental in enhancing the shear bond strength over that of the pristine poly (methyl methacrylate), consequently resulting in superior adhesion with the teeth [09Ata].

8.4.1.2 Conducting

The polymers with low glass transition temperature like silicone rubber gel are employed as electronic potting [97Pec]. This method involves filling up of electronic assembly with polymers which impart shock resistance and vibration damping together with exclusion of moisture or any other corrosive materials with the aid of adhesives having low viscosities [97Pec]. The conductive adhesives are used in smart card, liquid crystal displays, and so on [98Sut]. These adhesives are generally formulated using a metal-containing polymeric resin, and thus the use of conducting C-based nanomaterial–polymer nanocomposites is promising in this milieu. The requirement of high electrical conductivity for circumvention of the gathered electrostatic charges brings forth the advantageous use of C-based nanomaterials in the adhesives. The carbon nanotubes supersede the cost-effective carbon black in enhancing the adhesive response of the polymer, apart from influencing their modulus and flame retardancy [10Byr]. The clay-based cyano ester thermosetting polymeric nanocomposites exhibit significant adhesive strength in addition to perk in physico-mechanical and thermal properties for aerospace structural adhesives [03Din].

8.4.1.3 Miscellaneous

The adhesives are used to fix in paper and textile industry, household materials, potteries, lidding-type adhesives for food items and their packaging, and laminating in automobile interiors, furniture, and so on [04Bau]. It is used as an adhesive in billboards, corrugated board, plywood, and wallpaper [04Bau]. The liquid glues; remoistening adhesives such as tapes, stamps, etc.; corrugating adhesives used to join the two layers of papers; hot-melt adhesives; adhesives used to making paper bags; or laminating adhesives used particularly for packaging applications are usually made up of starch or dextrin with incorporation of mineral fillers [04Bau]. The use of clay in this vein in lieu of other fillers used seems promising to enhance the adhesive strength. According to an estimate of the various adhesives used in the USA presented in the book entitled *Bio-Based Polymers and Composites*, the lion's share in this vein comprise of the formaldehyde-based adhesives, followed by thermosetting and thermoplastic polymer-based, latex-based, and isocyanate-based adhesives [11Woo]. The urea–formaldehyde and phenol–formaldehyde adhesives are used in construction and furniture like plywood, fiberboard, wood particle board, etc. [94Bau, 11Woo]. Lei et al. reported enhancement of the adhesive strength of urea–formaldehyde resin upon formation of formaldehyde–clay nanocomposites [08Lei]. While the X-ray diffraction study showed exfoliation of the clay platelets during acid curing of the resin, the differential scanning calorimetry confirmed the catalytic effect of clay in accelerating the curing of the resin to result in a controlled cross-linking density with formation of hardened cure set [08Lei]. Apart from influencing the adhesive property of the resins, the inclusion of clay improved the water-resistance and thermal properties of the formaldehyde resins [08Lei]. The latex-based adhesives find uses ranging from packaging to textiles and furniture, and the use of latex–clay nanocomposites as adhesives dates back to the mid-1980s [08Val].

The polymers used as laminating adhesives include poly(vinyl acetate), poly (vinyl alcohol), styrene-butadiene rubber latex, starch, acrylic emulsions, low- and high-density polyethylene, polypropylene, and so on [90Iov]. The clay nanocomposites of the aforementioned polymers possess superior adhesive property for use as paperboard for packaging applications.

8.4.2 Coating and Paint

8.4.2.1 Automotive

Varnishes are solvent-thinned amalgamation of drying oil and resin, which are extensively employed in coating the body of vehicles [99Lam]. The coatings in automobile industry include engine enamel, underbody area, and so on, and the prime requirements of these coatings are resistance to grease and durability [99Lam]. The use of C-based nanomaterial-based polymeric nanocomposites as self-healing materials teaches us to exploit the same as shape memory paints and coatings for the automobiles to impart resistance to crack and facilitate scratch recovery upon damage by heating the film above its T_g [11Pot].

In special applications like aerospace industry, the size scale, aspect ratio, and properties of nanotubes provide advantages in a variety of applications, including electrostatically dissipative materials; advanced materials with combined stiffness, strength, and impact for aerospace or sporting goods; composite mirrors; and automotive parts that require electrostatic painting and automotive components with enhanced mechanical properties [02Par, 09Lee]. The clay–polymer nanocomposites possess pronounced dimensional and thermal stability and flame retardancy, which are prime requirements in commercial aircrafts and space vehicles [11Mee].

The thermal softening, creep, and decomposition of the polymeric matrix deteriorate their performance in automotive industry [94Max]. These problems of softening and delamination or cracking confronted by the polymeric films forward the replacement of the same by their clay- or C-based nanomaterial–polymer nanocomposites. Thakur et al. reported the use of graphene oxide-based hyperbranched polyurethane nanocomposites as shape-memory coating materials, which find major applications in automobile industries [14Tha]. In context to the safety of the human, daylight fluorescent paints are used for the warning against the nearby hazard or for display purposes [99Lam].

8.4.2.2 Marine

These coatings are used in ships, dock, and harbor installations, and offshore structures. Unlike others, the limited prospects for application of the paint to these macrostructures in service form the major hurdle in painting ships [01Hic]. The conventional paint comprising of the primer, undercoat and finishes, or topcoat is used, but the paint requirements vary for the two different portions of the ship, viz., superstructure and hull portion [01Hic]. The paint formulation differs even for the different hull portions of the ship, viz., top, boot, and bottom portions. The durability of these paints is of prime concern because regular maintenance of such large structures is troublesome [01Hic]. The primer and topcoat are used for the superstructures wherein resistance to salt, intensive sunlight, or rain is of prime concern [01Hic]. The zinc phosphate in medium oil alkyds or epoxy esters is employed as the primer [01Hic]. A number of polymers are used in this context like vinyl and chlorinated rubber and two-pack epoxies or polyurethanes [01Hic]. The poor adhesion property of the rubbers instigates the use of epoxies for the same. However, the uncontrolled oxidation and chalking formed due to excessive cross-linking of the epoxy resins poses a major problem [04Mal]. The major hurdle in the use of the epoxy resins for underwater applications is their moisture absorption due to their polar nature, which consequently lessens their physico-mechanical performance and toughness [09Kar]. In this context, the use of hyperbranched polymers and nanomaterials in modulation of cross-linking density of the epoxides sounds promising [09Kar]. The afore-stated problems are shorted out by using clay–epoxy nanocomposites which impinges favorable barrier properties and reduces their moisture absorption for use in naval applications [14Bar]. While the prime requirements for the top portion of the hull being good adhesion to the primer and ability to withstand thrust exerted by the sea waves, the boot portion seeks the resistance to salt water and abrasion in wet conditions and antifouling property for the bottom portion [01Hic]. The two-pack polyurethane is commonly used in the topcoat enamels with OH-containing saturated polyester as the paint base and isocyanate as the cross-linking agent [01Hic]. The one-pack chlorinated rubber and vinyl resins are also used as the enamel material for the topcoat [01Hic]. The problem of fouling of the ship bottom is another formidable problem apart from its durability [01Hic, 07Alm]. The coal tar is commonly used for the bottom paints where aesthetic appearance is not important relative to the performance to bring in good oil or chemical resistance [00Ras]. The fouling activity by the marine fauna and organisms results in causing an increased drag on the vehicle and consequently leads to higher fuel consumption in addition to bringing forth the onset of corrosion [07Alm]. The need for the attainment of the good adhesive, mechanical, chemical resistance and antimicrobial properties for high-performance paint formulations in the hull portion of the ship can be tackled by inclusion of nanomaterials like C-based nanomaterials [08Bei]. The conventionally employed tributyltin oxide, organotin, or triphenyltin derivatives are toxicants which decay at the logarithmic rate in the water bodies and pose hazard to the useful aqueous flora and fauna [03Oma, 08Lad]. The properly modified clay can also suffice the need for the same [10Lin]. The use of these nanomaterials unlike the conventional copper- or tin-based antifouling additives in the marine paint formulations addresses the basic water pollution or toxicity problems confronting marine organisms as well as human [08Bei].

8.4.2.3 Building Decorative

The building or architectural decorative coatings are protective, and pigmented enamels which form durable films to adhere to, hide, and protect the surface [99Lam]. Cover-up and decoration are the two jewelleries worn by the paints [99Lam]. The gloss or specular reflection is a function of refractive index of the coating material [01Tre]. In this context, it is pertinent to cite for evidence, the use of high-refractive-index phenolic resins that are useful as the high-gloss paints as compared to the low-refractive-index poly(vinyl acetate)-based paints, provided the surface to be coated has a smooth texture [98Sto]. The clay- and C-based nanomaterials play the significant role of driers to lessen the film drying time, mildewcides to impart antifungal activity, and as thixotropic agents to reduce settling or sagging of the pigment particles by conferring thixotropic consistency to the wall paints and coatings. Polyurethane coatings are organic in nature and thus prone to degradation by environmental influences like ultraviolet (UV) light, moisture, dust, oxygen, water, and so on [02Yan]. These factors alter the chemical structure of the polyurethane and cause deterioration in the physical (which includes loss of gloss, cracking, blistering, and so forth) and mechanical (reduction in tensile strength, elongation at break or brittleness, and so on) properties of the film [02Yan]. In this vein, Nuraje et al. report that graphene equips polyurethane topcoatings to resist environmental degradation, particularly ultraviolet light and corrosion [13Nur]. The incorporation of graphene improves the physico-mechanical properties of polyurethane apart from acting as an UV screener which absorbs UV light and hinders the same from degrading the polymeric surface [13Nur]. These graphene-based polyurethane nanocomposites are superior over other nanomaterial-based polymeric nanocomposites owing to the unique properties of C-based nanomaterials [13Nur]. The improvement of hydrophobicity of graphene-polyurethane nanocomposites merits a special mention in context to retarding of degradation process caused due to weathering by moisture [13Nur]. The acidified clay–epoxy nanocomposites are suitable for cost-effective protective and decorative coatings. The toxicity and high cost of long-chain alkyl ammonium salt-modified clay forward the use of acid-modified ones in new frontiers of the decorative technology [08Pai].

The decorative paints are of several types depending on gloss index, viz., matte, semigloss, gloss, and fully gloss [99Lam]. While the former reflects no light and is used to hide imperfections as in outside boundary walls, the others exhibit smooth coating which reflects light incident on its surface for use in the home interiors and kitchen or food processing area. The abovementioned nanomaterials play a significant role in enhancing the gloss characteristics of the coatings, apart from increasing their chemical resistance.

Indoor Paint

The gloss enamels (having 90–98+ gloss at 60° angle of incidence) are particularly used in indoor coatings as they can dry to result in highly reflecting surface [99Lam]. The poor fire resistance of the polymers including epoxy forms the major drawback in their practical utility [02Yan]. In this vein, the clay- or C-based nanomaterial–polymer nanocomposites possess improved gloss and address the above problem, thereby resulting in flame-retardant coating materials. These nanomaterials work as flame retardants by the formation of char with either carbonaceous or multilayered silicate structure in the condensed phase upon burning, which forms a protective coating onto the film surface and insulates the material coated underneath [10Kil, 13Dit]. The non-evolution of toxic gases unlike other flame-retardant additives justifies their contribution toward sustainability.

Outdoor Paint

The prime concern in the use of paints for outdoor applications is to obtain a protective finish and to guard against the deleterious effect of solar radiation, rainfall, dust, moisture, temperature, and many other environmental factors [99Lam]. The waterborne paints are generally recommended for use in external purposes where heavy wear and tear occurs. The nanomaterials possess resistance to corrosion, solvent, or any external factors and thus enhance the durability of the polymeric nanocomposite coatings [99Lam]. In this regard, the modification of clay with or functionalization of the C-based nanomaterials with benzotriazole or triazine derivatives prior to incorporation into the polymeric matrix seems promising technique to impart photostability to the paints [95Vat]. The flat (having 4–5 gloss at 60° angle of incidence) or semigloss (having 20–60 or 80 gloss at 60° angle of incidence) house paints or enamels are used for outdoor applications as they dry to a non-glossy mat surface [99Lam]. The polyamide modified alkyd resins find their utility as architectural and maintenance paints.

8.4.2.4 Textile

The coated fabrics are extensively employed as roofing materials in tents, hanging roofs, and many such wide-span surface materials of lightweight in structure [99Lam]. The environmental factors like wind, rain, snow, and so on exert stress on the roofing materials which acts biaxially. Asphalt is the common roofing materials used till date [65Hen]; however the inclusion of silica, talc, dolomite, and so on into the same renders shatter- and shockproof roofing systems in cold countries [82Hen]. In this vein the use of clay is envisaged to suffice the need at minimal loadings as compared to the conventional fillers used.

The use of nanocomposites of C-based nanomaterials surrogates the electrically conducting coatings and suffices the need as nonmetallic textile paints and coatings [08Per]. Spur from the fact that the coating of C-based nanomaterials on textile fabrics affords antimicrobial activity, Pramanik et al. fabricated an efficient coating material for textiles [13Pra1, 14Pra1]. The report highlights the use of diethanol fatty amide of castor oil functionalized multiwalled carbon nanotube–hyperbranched poly (ester amide) nanocomposites as coated fabrics in textile industries. The nanocomposites possess antibacterial efficacy, antistatic property, and thermostability [13Pra1, 14Pra1]. These nanocomposites overcome the troubles relating to the burst discharge of the antibacterial agents compared to the conventional systems. The nanocomposite film possesses antistatic property and hence avoids the buildup of static electrostatic charges causing electric shocks and fire hazards [13Pra1]. These nanocomposites surmount the limitations associated with the conventionally existing antistatic agents such as blooming/blushing, moisture dependency, and so on. Further thermostability of the films is relevant in context to the melt-spinning processability of the textile materials [13Pra1]. These nanocomposites thus epitomize an efficient non-leaching antibacterial, antistatic, and thermostable coating material for use in textiles.

8.4.2.5 Biomedical

An emerging research in the arena of clay- and C-based nanomaterial–polymer nanocomposites is focused on their biomedical applications. In this vein, the nanocomposites of bio-based hyperbranched poly(ester amide) using polyaniline nanofiber-modified clay find use as antimicrobial coating material for use in the biomedical domain [14Pra2]. The nanocomposites exhibited acceptable physico-chemico-mechanical properties apart from antimicrobial attributes [14Pra2]. The report documented that the interplay between the nanofibrous polyaniline chains and partially exfoliated nanoplatelets of clay in the nanocomposites forms the rationale behind the pronounced antimicrobial activity against a spectrum of bacterial and fungal strains and an algal consortium [14Pra2]. Hydrogels are basically used in biomedical coatings owing to their biocompatibility with the body tissues or organs. The adsorption of poly(vinyl alcohol) chains in between the graphene oxide nanoplatelets helped cross-link a biocompatible hydrogel [10Bai]. This study attested the use of such graphene oxide-based hydrogel nanocomposites in surgical coatings and controlled drug delivery, particularly vitamin B12 depending on the surrounding pH. The biocompatible poly(oxyethylene sorbitan laurate)–graphene oxide nanocomposites are used as freestanding films in surgical implants or transplant devices [10Bai]. Research findings have reported the incorporation of graphene oxide into biocompatible and biodegradable chitosan and polylactide matrices improved their performance, which forwards these nanocomposites to expand their utility in different biomedical sectors which are otherwise limited owing to the poor mechanical properties of the pristine polymers [11Pan, 12Mar].

8.4.2.6 Electronic

The polymeric nanocomposites using C-based nanomaterials seem promising to obtain a multimodal paint system with extraordinary mechanical, electrical, and thermal properties. The intumescent clay-based polymeric nanocomposite coatings possessing significant heat distortion temperature and pronounced barrier and mechanical and flame-retardancy properties find uses in flame-retardant low-voltage wires and cables [07Wan2]. The "contact sport" between zero- and C-based one-dimensional nanomaterials was explored in this vein. The inclusion of silver nanoparticles decorated multiwalled carbon nanotubes into bio-based polymeric matrix resulted in sustainable coatings for electronic applications [14Pra1]. The nanocomposites possessed adequate antistatic property and thermostability for use in the domain of electronics [14Pra1]. The antibacterial activity against a number of Gram-positive and Gram-negative bacterial strains forwarded the same for special applications in biomedical electronics [14Pra1].

In a nutshell, the spectrum of applications of clay- and C-based nanomaterial–polymer nanocomposites as adhesives, paints, and coatings is represented schematically in Fig. 8.2.

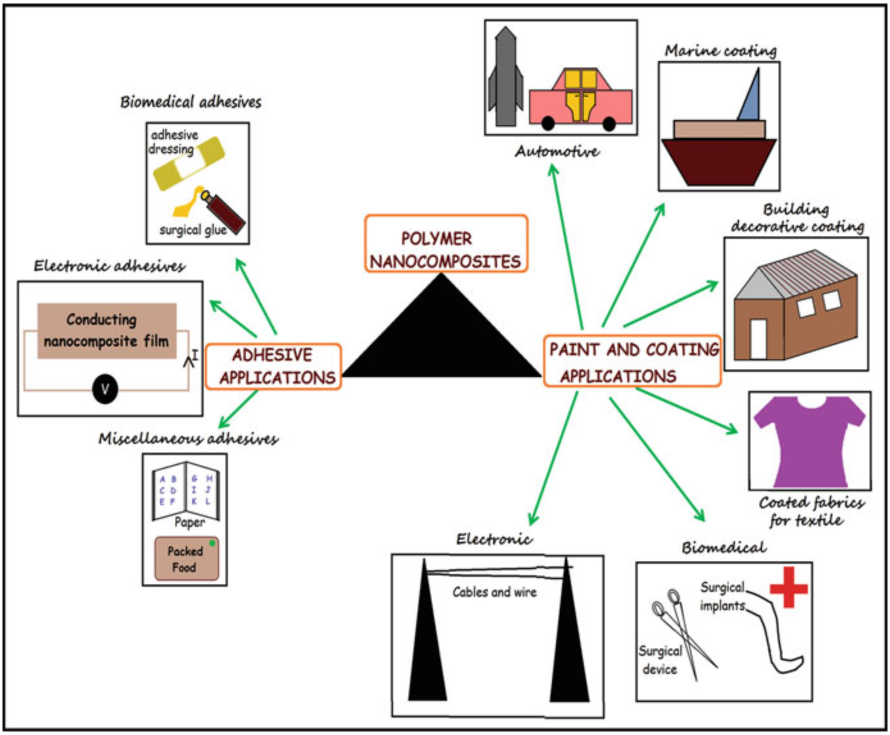

Fig. 8.2 Utility of clay- and C-based nanomaterial–polymer nanocomposites as adhesives, paints, and coatings across different domains

8.5 Conclusion

The advantages of the inclusion of materials at nanoscale regime in the polymeric matrix have opened myriad opportunities for the polymeric nanocomposites, especially based on clay- and C-based nanomaterials in varied commercial applications. The demand for the materials in the horizons of advanced adhesives, coatings, and paints is beginning to drive in revolutionary interests and advances, although not involvement, and thus these potential technologies continue to remain at their infancy. The clay- and C-based nanomaterial–polymer nanocomposites are one of the technologically promising innovations in recent times. However, the C-based nanomaterial–polymer nanocomposite technology is yet to flourish as the contemporary clay-based polymeric nanocomposites one. The technology developed in recent times begs to be utilized in every possible way, but these nanotechnology initiatives are simply to be found in laboratories and have not been extended to industry at pilot scale. There is an urgent effort to bridge up the advanced high-tech solutions from bench to bedside. Industrialists are hedging and are scared of taking the risk of implementing a new technology and hence are dabbling in the field. The industries need to continuously upgrade their technological skill sets, collaborate or network with the expertise in the relevant fields, and implement their recent research findings to keep their pace with their competitors.

Although the alkyds and many other polymeric resins undoubtedly continue to hold a strong foothold in the paint and allied industries, the stride toward the use of clay- and C-based nanomaterial-based polymeric nanocomposites in the same domain is envisaged to reach the pinnacle in recent future. The issues relating to the success of using the clay- and C-based nanomaterials in polymeric nanocomposites will be embraced by their marketplace. The concern over the environmental pollution has sparked up a debate in context to the use of polymeric nanocomposites – a boon or ban? However the magic lies in the hands of the material scientists to tune the surface functionalities of the nanomaterials for achieving the desired potentiality.

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Polymer Nanocomposites for Shape-Memory Applications

9

Tuhin Chatterjee and Kinsuk Naskar

9.1 Introduction

9.1.1 Smart Materials

The ability of materials to sense and respond to external stimuli that enables these materials to change their properties, such as shape, color and electrical conductivity, as a result of pH, temperature, chemicals, light, or stimulation by an electric or magnetic field, has eminent scientific and technological importance. This prominent feature truly makes them "smart" and the materials that respond dynamically to external stimuli are called intelligent or smart materials, and it is important that their response should be repeatable and controllable. Fast macroscopic changes occurring in the structure of the smart materials are not only responsible for this unique characteristic of the materials, but some of the shape changes are also reversible. Such smart behavior of smart materials is different from smart systems or facilities because smart materials are intrinsically sensitive to changes in their ambient environment instead of relying on the complicated sense-response structure of the feedback system [07Liu].

Applications of smart materials in the field of material science have achieved outstanding result due to their proficiency of executing unique functions in response to changes in stimuli and hence have promising applications in many areas, for instance, as actuators, sensors, and micropumps. Few smart materials (SMs) have the capability to move effectively on applying a precise stimulus. Depending upon the response of smart materials to external stimuli, smart materials can be further classified into two subgroups: shape-memory materials (SMMs) and shape-changing materials (SCMs).

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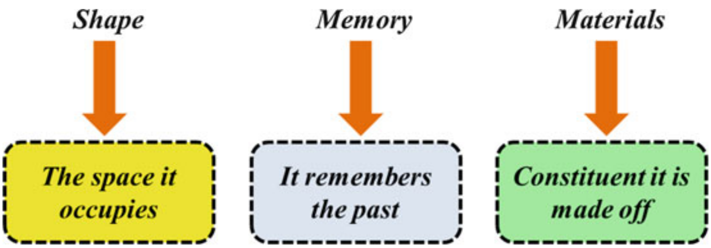


Scheme 9.1 Schematic representation of shape memory materials

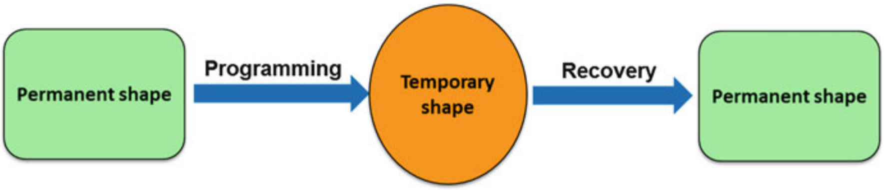


Fig. 9.1 Schematic representation of shape memory materials

9.1.1.1 Shape-Changing Materials (SCMs)

Generally, SCMs shrink or bend, as long as they are exposed to an appropriate stimulus, and the recovery to its original shape is possible after elimination of stimulus. Without application of any stress, a SCM can change its shape several times. Principally, heat and light are the most commonly used stimuli for SCMs. Particularly, light is the fascinating stimulus because of its modulation in terms of wavelength, polarization direction, intensity, etc. Presence of functional groups like cinnamic acid or azobenzenes makes a material light responsive [13Iqb].

9.1.1.2 Shape-Memory Materials (SMMs)

A promising class of smart materials that can remember the past is shown in the Scheme 9.1. SMMs have the ability to memorize a permanent shape, be programmed and fixed to a temporary shape under specific conditions of temperature and stress and later relax to the original state upon exposure to an external stimulus such as heat, light, electricity, magnetic field as depicted in the Fig. 9.1.

As one of the most important branches of smart materials, shape-memory materials (SMMs) can also be classified into three categories which include:

(a) Shape-memory alloys (SMAs)
(b) Shape-memory ceramics (SMCs)
(c) Shape-memory polymers (SMPs)

Over shape-memory alloys (SMAs), shape-memory polymers (SMPs) have the following advantages which are given Table 9.1.

Table 9.1 Comparative study between SMPs and SMAs

(SMPs)	Properties	(SMAs)
0.9–1.2	Density (g/cm^3)	6–8
Up to 800	Extent of deformation (%)	<8
1–3	Required stress for deformation (MPa)	50–200
<200 °C, low pressure	Processing conditions	>1000 °C, high pressure
1–3	Stress generated upon recovery (MPa)	150–300
Can be biocompatible and biodegradable	Biocompatibility and biodegradability	Some are biocompatible but not biodegradable
Low	Cost	High

9.1.2 Shape-Memory Polymers (SMPs)

Regular polymers response to external stimuli (like softening of materials at higher temperature) gradually and that response is linear in nature. Shape-memory polymers (SMPs) or stimuli-responsive polymers (SRPs) behave differently to those external stimuli and even a small magnitude of external stimuli imparts significant changes in the shape, size, color, and conductivity of SMPs. But the response of SMPs to external stimulus is very rapid and nonlinear in nature.

SMP exhibits a radical change from a normal rigid polymer to a very stretchy elastic and back on command, a change which can be repeated without degradation of the material. The "memory," or recovery, quality comes from the stored mechanical energy attained during the reconfiguration and cooling of the material.

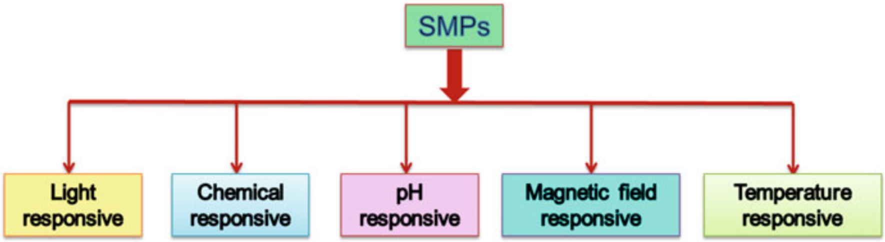
The most common conventional SMP systems include cross-linked PE and PE/Nylon6 graft copolymers, trans-polyisoprene (TPI), cross-linked ethylene vinyl acetate copolymer, styrene-based polymers, acrylate-based polymers, polynorbornene, cross-linked polycyclooctene, epoxy-based polymers, segmented polyurethane (PU), and segmented PU ionomers. Additionally, some new biopolymers like poly lactic acid (PLA) poly(3-hydroxyalkanoate)s (PHAs) have been developed to exhibit SME [08Rat].

Based on the nature of the external stimulus, SMPs can be categorized into five categories which are given in the Scheme 9.2.

Among all the categories, thermal- or temperature-responsive SMPs are much more popular.

9.1.2.1 History of SMPs

The term "shape-memory" was first proposed by Vernon in 1941. However, the importance of SMPs was not recognized until the 1960s, when cross-linked polyethylene (PE) was used for making heat-shrinkable tubes and films. More efforts to develop SMPs began in the late 1980s, accelerating in the 1990s and making significant progress only in the past 5–10 years. The main focus of the earlier works in shape-memory polymers was the development of new materials for various end use applications. In that case, fundamental enquiry was not so much and few



Scheme 9.2 Schematic diagram of various shape memory polymers

thermomechanical properties were tuned only. Recently, these materials have gained interests in academic field for more tailored applications.

9.1.2.2 Advantages of SMPs

(a) In addition to thermal stimuli (heating), various external stimuli (e.g., light, magnetic field, chemical, electricity) can be used to trigger the shape recovery. Even the coexistence of the different stimuli leads to the multisensitive materials.
(b) They exhibit highly flexible programming and the programming can be done through single and multistep processes with various stimuli.
(c) Range of structural designs for SMPs is very broad. Various polymers and foreign materials can be used to develop different SMPs. Additionally, there is an abundance of approaches for designing net points and switches for different kinds of SMPs.
(d) Properties of SMPs can be tuned easily and accurately through the formation of composites, by blending of two different polymers even by the synthesis methods also.
(e) Few SMPs are well suited for responses to human tissues and hence biocompatible and in some cases biodegradable also. Biocompatibility and biodegradability of SMPs provide an abundant array of choices for making highly comfortable devices to interface with our bodies, biological and garment-integrated devices, and also offer unique opportunities for development of smart materials.
(f) In spite of occupying large volume SMPs are very lightweight material which is extremely important for applications such as aerospace devices, aeroplane components, air force items, etc. [12Hu].

9.2 Fundamental Principles of SMPs

Before moving to the fundamental aspects of the SMP mechanism, key terms and techniques which are used to describe and characterize the SMP behaviors are summarized below.

Transition Temperature (T_{trans}): T_{trans} that could be the melting temperature (T_m) or glass transition temperature (T_g) is the temperature around which a shape-memory material changes from one state to another state.

Shape Fixing Components: In a SMP network, shape fixing components are defined as domain or net point which maintains the dimensional stability during deformation and recovery. These net points are generally either physically cross-linked (physical entanglement or H-bonding) or chemically cross-linked.

Shape Fixing Components: Usually polymer chains in the SMP networks act as shape switching components which can switch from one state to a different state in response to the stimuli.

Shape Deforming Temperature (T_d): Temperature at which SMP is strained to a temporary shape. T_d has significant impact on the shape-memory behavior of an SMP.

Shape Fixing Temperature (T_f): Working temperature at which the temporary shape of a deformed SMP is fixed. Generally, T_f is lower than the T_{trans}.

Shape Recovery Temperature (T_r): It is defined as the temperature at which an SMP is triggered to recover its permanent shape from its deformed shape. Usually T_r is higher than T_{trans}.

Recoiling of the polymeric chains from a strained configuration (temporary state) to a less-strained configuration (memorized state) which is also called the "entropy elasticity" is the driving force for the shape recovery of SMPs. The "memorized" state is the most relaxed, equilibrated configuration of the materials. The original orientations of the chain segments become altered upon deformation at a higher temperature ($T > T_{trans}$), and the dislocation of the net points also take place which results in the formation of a new set of local chain-chain interactions. Upon cooling ($T < T_{trans}$) this temporary shape can be fixed, because the newly formed chain-chain interactions are strong enough to overcome the tendency of elastic recoiling of the chain segments. Again upon triggering to a higher temperature ($T > T_{trans}$), the increased entropy of chain segments overcomes the local chain-chain interactions and allows the elastic recoiling of chain segments to a more disordered state as shown in the Fig. 9.2.

The net points, which provide the dimensional stability to a SMP network, are either covalently or physically cross-linked. The switching components may be either amorphous or semicrystalline and reversibly respond to the temperature changes. Based on the net points and switching components, SMP can be classified into four categories:

(a) Chemically cross-linked net points with amorphous switching components
(b) Chemically cross-linked net points with semicrystalline switching components
(c) Physically cross-linked net points with amorphous switching components
(d) Physically cross-linked net points with semicrystalline switching components

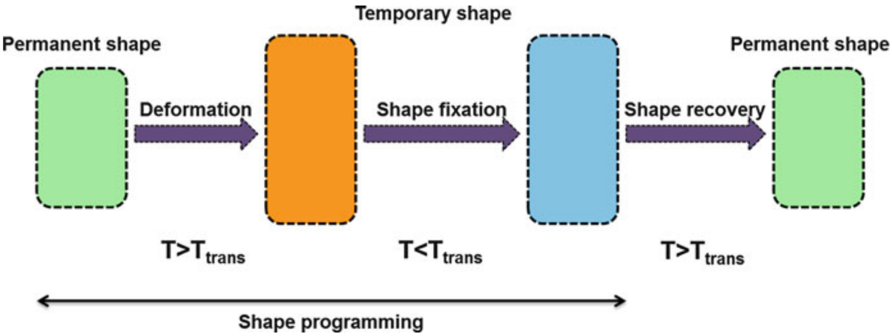


Fig. 9.2 Schematic representation of thermally induced shape-memory effect

The first two belong to the thermoset SMPs and the last two belong to the thermoplastic SMPs. Chain entanglements or local crystalline domains formed by strong chain-chain interactions serve as a physical cross-linking sites for thermoplastic SMPs. The main advantages of thermoplastic SMPs include the ease of moldability with different permanent shapes/configurations, high shape deformation range, and the ease of blending with other polymers and additives. On the other hand, in thermoplastic SMPs the original network points could be destroyed during the deformation because of the temperature dependency of the physical cross-links, which results in incomplete shape recovery in case of thermoplastic SMPs.

In contrary to thermoplastic SMPs, chemically cross-linked SMPs means thermoset SMPs exhibit better strain recovery ratios and strain fixing ratios together with faster strain recovery rates and larger shape recovery stress. Higher cross-linking densities and the ability of chemical cross-links to withstand tensile deformations result in the combination of the above properties in case of thermoset SMPs. After chemical cross-linking, incapability to be reprocessed into a new shape/configuration is the main disadvantage of thermoset SMPs. The incapability to reprocess a chemically cross-linked SMP is not a matter of concern where the SMPs are designed for a one-time application.

An ideal SMP system may be designed at the interface of thermoplastics and thermosets. Appropriate choice of the processing programs, optimization through rational molecular and network designs, is the key parameter for the development of successful, application-driven design SMPs. In essence, the shape-memory property is a combination of thermal and mechanical properties.

9.3 Molecular Mechanism of SMPs

To exhibit shape-memory functionality, a material should be stable in the deformed state in a range of temperature which is relevant for the particular application. A material can gain the above function by using the network chains as a kind of molecular switch, and the flexibility of the chains should be a function of temperature. At temperature above T_{trans} the chain segments become flexible, while below

T_{trans} the flexibility of the chain segments is limited to some extent. If melting point (T_m) is chosen as a thermal transition for the fixation of the temporary shape, strain-induced crystallization of the switching segment can be started by cooling the material. Though the crystallization is always incomplete, the crystallites which is formed prevent the segments to reform the coil like structure immediately and also prevent the spontaneous recovery to the permanent shape. The permanent shape of shape-memory networks is stabilized by covalent net points, whereas the permanent shape of shape-memory thermoplastics is fixed by the phase with the highest thermal transition [12Sun].

Various kinds of structures and programming models have been proposed to explain the mechanism of SMEs of SMPs. The molecular mechanism of programming the temporary form and recovering the permanent shape of thermal-sensitive SMPs is demonstrated in the Fig. 9.3, where the glass transition temperature (T_g) is considered as the transition temperature for the polymer network.

With rise of temperature $T > T_{trans}$ of the switching segments, the segment becomes flexible and the polymer can be deformed elastically. Cooling down to temperature $T < T_{trans}$, a temporary shape can fixed. Again reheating of the segmental chains helps to recover the permanent shape. On the other hand, a supramolecular system tends to adopt its architecture in response to environmental conditions such as change of temperature due to the labile nature of noncovalent interactions which generates a novel shape-memory mechanism model as shown in Fig. 9.4.

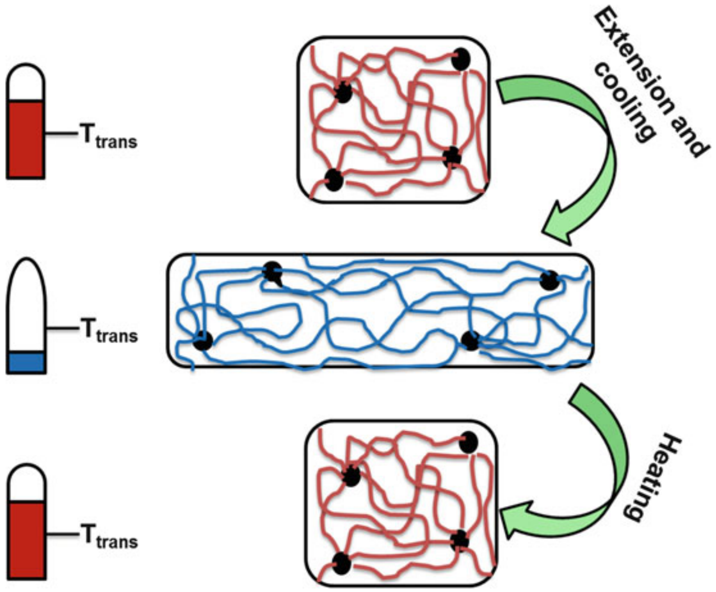


Fig. 9.3 Schematic representation of the molecular mechanism of the thermally induced shape-memory effect of a polymer network

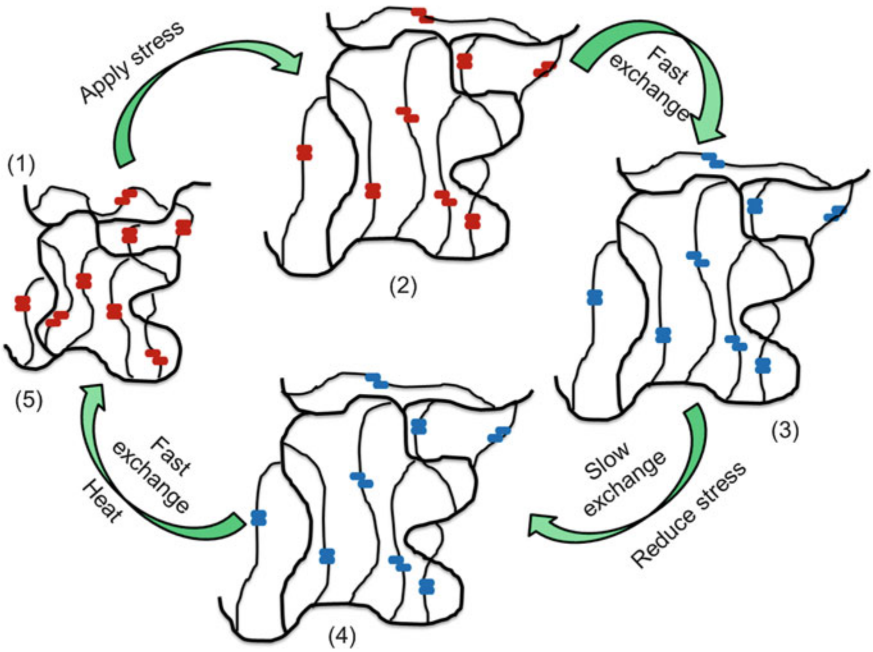


Fig. 9.4 Molecular models of SMEs involving thermal reversible supramolecular switches

For supramolecular SMPs, The above mechanism involves thermoreversible quadruple hydrogen-bonding (H-bonding) side groups in an elastic polymeric network [97Lia, 12Hu].

9.3.1 One-Way Shape-Memory Effect (SME)

One-way SME features a chemically or physically cross-linked structure which is capable of memorizing its permanent shape, and in this case the glass transition temperature (T_g) or melting temperature (T_m) is considered as a “switching” temperature or “triggering” temperature which is also called the “transition” (T_{trans}) temperature. Above the T_{trans}, upon application of stress the constituent network chains gain enough mobility to allow significant and reversible deformation. After that, if the deformed sample is cooled below T_{trans} the same network chains become highly constrained as a result of the fixing of the deformation such that the deformation remains even after the stress release also. In this condition, the material exists in a dormant or metastable state. Again reheating of the material above T_{trans} imparts mobility to the constituent polymer chains and hence shape recovery of the sample takes place driven by entropic elasticity. The main features of the one-way SME is that only the recovery step (e.g., length contraction) is spontaneous, while the deformation step (e.g., elongation) requires external intervention involving force application to overcome the entropic elasticity [96Kim].

9.3.2 Two-Way Shape-Memory Effect (SME)

In this case, the material shows the shape-memory effect during both heating and cooling. This means that the material remembers two different shapes: one at low temperature and the other one at high temperature. The uniqueness of two-way SME is that during deformation no external force is needed. However, a material can be "trained" to "learn" to behave differently in two different conditions. Under normal circumstances, SMPs remember its high temperature shape while upon heating to recover its high temperature shape it "forgets" its low temperature shape immediately. Training enables the SMPs to 'remember' to leave some reminder of the deformed low-temperature condition in the high temperature phase.

9.3.3 Triple Shape-Memory Effect (SME)

In case of triple shape-memory effect (SME), material will switch from one temporary shape to another shape at the first transition temperature, and then at another higher temperature back to the permanent shape. Combination of two double-shape-memory polymers with two different T_g's shows triple SME [10Xie].

9.4 Shape-Memory Polymer (SMP) Nanocomposites

The development of polymer nanocomposites is very much promising from industrial and scientific point of view. Polymer nanocomposites are very much useful to improve the stiffness, mechanical properties, barrier property, fire retardancy, and dimensional stability. Nowadays, SMP nanocomposites are the matter of concern in order to improve the properties or to obtain new functions of SMPs. The preparation of SMP nanocomposites is mainly for five reasons:

(a) To improve shape recovery stress and mechanical properties
(b) To decrease shape recovery induction time by increasing thermal conductivity
(c) To create new polymer/polymer blends with shape-memory effect (SME)
(d) To tune switch temperature, mechanical properties, and biomedical properties of SMPs
(e) To fabricate shape-memory materials sensitive to electricity, magnetic, light, and moisture

SMP composites and blends exhibit novel properties that are different from the conventional SMPs and thus can be utilized in various applications [09Men, 10Mad].

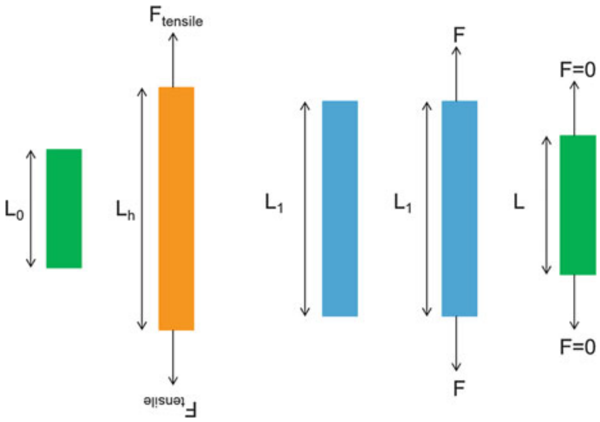


Fig. 9.5 Schematic representation of the steps of shape-memory testing

9.4.1 Thermomechanics of SMP Nanocomposites

The so-called cyclic thermomechanical test as shown schematically in Fig. 9.5 is performed to characterize the shape-memory functionality of SMP nanocomposites. Dynamic mechanical analyzer (DMA) and tensile testing machine attached with a temperature-controlled chamber is used together to determine the shape-memory properties.

A test specimen of SMP nanocomposite with original length (L_0) is started heating from room temperature to above a transition temperature, which may be the glass transition (T_g) or melting transition (T_m). Then the test specimen is elongated to a certain strain (L_h) by application of an external force $F_{tensile}$. The new shape is then fixed by cooling the constrained specimen below its shape fixing temperature which again may be T_g or crystallization temperature (T_c). After that, upon release of the load, instantaneous shrinkage of the test specimen from length L_h to L_1 will take place as the sample is cooled [07Cao, 08Cao].

Shape Fixity Test

The sample length in the above three stages are used to determine the shape fixity (f) which is given in the Eq. 9.1:

$$f = \frac{L_1 - L_0}{L_h - L_0} \tag{9.1}$$

Value of $f = 100\ \%$ indicates no shrinkage of the test specimen upon release of the load. Sample length L_1 is then used for shape recovery test in DMA.

Shape Recovery Test

Heating of the sample helps to recover the permanent shape. In the first stage of the heating cycle, force (F) required to inhibit the shape recovery is monitored keeping the sample length L_1 same. Value of F implies the shape recovery stress.

In the second stage of the heating cycle, recovery to the original length of the sample is allowed against no external force ($F = 0$) and finally the sample length (L) is recorded. Hence, the recovery ratio (R) is determined by the Eq. 9.2 as follows:

$$R = \frac{L_1 - L}{L_1 - L_0} \tag{9.2}$$

For an ideal SMP, nanocomposite R = 100 %.

9.4.2 Various Kinds of SMP Nanocomposites

9.4.2.1 Carbon Nanotube (CNT) or Carbon Nanofiber (CNF)/SMP

Outstanding mechanical strength with high elastic modulus and high aspect ratios make CNTs and CNFs effective in improving the mechanical properties and shape recovery stress of SMPs. Incorporation of CNTs/CNFs as fillers in SMP matrix also results potential electrical and infrared-light-active SME of the prepared SMP nanocomposites. In some cases, CNTs/CNFs hamper the crystallinity of the matrix phase due to the poor dispersion of the CNTs/CNFs into the matrix. Even the different sizes of CNTs/CNFs have different influences on the crystallinity of the matrix. Therefore, chemical functionalization or oxidation of CNT/CNF surface or in situ polymerization leads to the better dispersion of the CNTs/CNFs into the SMP matrix phase.

Fabrication of CNF/shape-memory polyurethane (SMPU) nanocomposite by melt mixing technique diminished the shape-memory behavior of SMPUs as a result of the interference of the CNFs on the crystallization of the soft segment of polyurethane matrix. SMP nanocomposites containing surface oxidized CNFs show better dispersion of CNFs in the polyurethane matrix, crystallinity, better tensile properties, higher shape recovery force than the SMP nanocomposites with untreated CNFs. Another way of fabrication of CNF/SMPU nanocomposite is solution mixing in a polar solvent followed by slow evaporation of the solvent. In this case, anisotropic distribution of the CNFs into the polyurethane matrix were obtained which results in an increment of rubber modulus by a factor of 2–5 along with improvement of shape fixity due to the enhanced strain-induced crystallization. Solution mixing process with ultrasonic distribution of CNFs is also a technique for fabrication of CNF/SMPU nanocomposite. Only 3.3 wt% loading of CNFs enhance the shape recovery stress of the nanocomposites almost twice than the pure SMPUs [06Jun, 09Men].

On the other hand, CNT-based nanocomposties can also be prepared after functionalization of CNTs. Functionalized (in aniline at high temperature) multiwalled carbon nanotubes (MWCNTs)/SMPU nanocomposites can be prepared by solution blending. In situ polymerization after chemical functionalization of MWCNTs is also a technique for developing MWCNTs/SMPU-based nanocomposites. The hard segment of polyurethane together with MWNTs helps to recover deformed shape, and CNTs also improve the shape recovery stress of

SMPUs. In addition to the SMPU system, CTNs can also be used to reinforce shape-memory polyvinyl alcohol (PVA). Modified (surfactant stabilized) CNTs/PVA shape-memory fibers were developed by coagulation spinning technique. Herewith, the recovery stress of the CNTs/PVA nanocomposite is very close to that of SMAs [00Hag].

Ultimately, it can be stated that incorporation of CNTs/CNFs into the SMP matrix is effective in improving the mechanical strength, stiffness, and recovery stress of SMPs. Shape-memory nanocomposites containing uniform dispersion of (1–5) vol% of CNTs/CNFs result in 50 % more recovery stress than that of pure SMPs. Above the percolation threshold (maximum limit), CNTs/CNFs deteriorate the properties of SMPs. Influences of nanoscale fillers on the shape-memory effect of SMPs vary depending upon the complexity of the preparation of nanocomposites. Even the ultimate product properties are significantly affected by various factors like particle size of filler and its distribution, aspect ratio of filler, matrix nature, interface between matrix and filler, as well as processing techniques.

9.4.2.2 Nanoclay/SMP

In certain circumstances, organically modified nanoclay is also a good candidate to prepare some functional nanocomposites with outstanding properties. Incorporation of nanoclay into the matrix of SMP also improves mechanical properties and shape recovery stress of SMPs. Sodium montmorillonite (Na-MMT) intercalated with macroazoinitiator (MAI), which has a hydrophilic poly (ethylene-glycol) (PEG) segment, has been used to develop poly (ethyl methacrylate) nanocomposite through in situ polymerization technique. In this nanocomposite, Na-MMT/PEG block linked to poly (ethyl methacrylate) which acts as a hard phase contributes to shape-memory behavior of the nanocomposites and also enhances the ultimate mechanical properties. Organoclay/SMPU nanocomposites were also synthesized in which the reactive clay on polyurethane chains imparts a new network that adds additional constraints to the chain motion of the hard segments of SMPU.

Polyhedral oligomeric silsesquioxanes (POSS) with cage like structure is another nanoclay that can be used to prepare nanocomposites. In principle, norbornyl-POSS having either cycloheyl (CyPOSS) or cyclopentyl (CpPOSS) corner groups is used. The size of the cylindrical domains of POSS nanoclay influences the shape-memory properties. Generally, POSS-reinforced nanocomposite shows two stages of strain recovery:

(a) Strain recovery relates to the polynorbornene relaxation in the norbornyl matrix which is very fast in nature.
(b) Strain recovery related to POSS-rich domains which are slow in nature.

Cellulose, the most abundant substance in nature, can be used to reinforce the SMPs. In case of nanocellulose-reinforced SMPU nanocomposites, a small amount of well-dispersed nanocellulose markedly enhance the stiffness of SMPs without affecting the shape-memory properties. Polar groups of cellulose have a strong interaction with the polyurethane matrix.

Therefore, it can be stated that, nanoparticles can effectively improve the shape recovery stress of SMPs. However, higher loading of nanoparticles (>3 wt%) hampers the shape-memory properties of SMPs. It is observed that nanocomposite with only 1 wt% loading of nanoparticles offers about 20 % higher recovery stress than that of pure SMPU. Another feature that should be kept in mind is that only physical filling of nanofillers into the matrix of SMPs has no significant influence on shape-memory properties and mechanical properties of SMPs. Rather the nanofillers, which show chemical interaction with SMP chains, show prominent effect in improving the shape-memory properties of SMPs [01Fu, 09Men, 10Mad].

9.4.2.3 Nano SiC/SMP

Although filler SiC can improve the elastic modulus of SMPs, it hampers the SME of SMPs even at a very low loading. Sol-gel method has also been used to incorporate nano silica from tetraethoxysilane (TEOS) into the SMPU matrix that results higher breaking stress and modulus of the SMPU nanocomposite. SiC nanopowder has also been used to reinforce the epoxy resin which results in an increment of the elastic modulus of the thermoset shape-memory epoxy resin. However, negative effect of SiC on the SME of SMPUs has also been observed as a result of a dramatic decrease of the crystallinity of the soft segment of SMPU [04Cho].

9.4.2.4 Carbon Black (CB)/SMP

Conducting carbon black (nanodimension) have broad applications in the field of electric & electronics industry. In terms of shape-memory behaviour, compare to CNTs & CNFs, carbon blacks (CBs) are not so much effective in improving shape recovery stress of the nanocomposites. Carbon blacks rather severely deteriorates the shape recovery of SMPs. CB/SMPU nanocomposites, prepared by solution mixing shows very poor recovery ratio and low shape recovery speed of SMPU as a consequence of the destroy of the crystallinity of the SMPUs [00Li1].

9.4.2.5 Other Inorganic Filler/SMP

Poly(D,L-lactide) (PDLLA) is also a good shape-memory biomaterial having good biocompatibility and biodegradability. PDLLA-reinforced hydroxyapatite shows much higher recovery speed and higher recovery ratios than pure PDLLA and it is also biodegradable and biocompatible [06Zhe].

Celite (composed of silica and alumina) has hydroxyl groups on its surface and this hydroxyl group coupled with SMPU matrix to form the nanocomposites. Only 0.2 wt% of celite content in the celite/SMPU nanocomposites remarkably improved the mechanical properties and shape-memory behavior of the nanocomposites where celite acts as a cross-linker [08Par].

9.4.3 Trend of Development SMP Nanocomposites

9.4.3.1 Electrical-Sensitive SMP Nanocomposite

Incorporation of electrical conductive elements into the thermal active SMPs imparts a certain level of electrical conductivity into the SMPs. Electroactive SMPU nanocomposite has been developed by insertion of MWCNTs, polypyrrole (PPy), and PPy-coated MWCNTs into the matrix of SMPU. Compared to MWCNTs or PPy alone, PPy-coated MWCNTs are found more effective to improve electrical conductivity. It has also been reported that addition of Ni powder into SMPU matrix leads to the improvement of electrical conductivity even in a weak static magnetic field. Later on, SMP nanocomposite based on styrene has been developed by reinforcing styrene matrix with MWCNTs, CB, and short carbon fiber (SCF). In the above nanocomposites, simultaneous filling of CB and SCF show synergism to improve the electrical conductivity. CB helps to form interconnection between the SCF, while the fibrous SCFs act as a long distance charge transporter by formation of a conductive network. It is also reported that the belt of a CNT/SMPU nanocomposite recovers its original shape from the deformed shape upon application of an electrical current. Hence, it can be demonstrated that through the conductive networks of SMPs when current passes internal temperature rises above the transition temperature to trigger the shape recovery as a result of induced joule heating.

Variation of temperature and strain that occurs during an electroactive shape-memory process has a noticeable influence on the electrical resistivity of the filled SMP. It is reported that imposed deformation of the CB/SMPU nanocomposites shows pronounced positive temperature coefficient (PTC) of resistivity as a result of the imposed deformation that can increase the resistivity of CB/SMPU nanocomposites by several orders of magnitude. In case of CNF and oxidized-CNF-filled SMPUs, strain did not significantly affect the PTC effect. In case of electroactive SMPs, influence of nanoconductive fillers also should be taken into consideration. In principle, fibrous conductive fillers enhance the electrical conductivity, stiffness, and strength of SMPs significantly than that of CBs. On the other hand, in comparison to conductive particles, bending strain is lower for fibrous conductive fillers and recoverable strain for fibrous filler-reinforced composite is also a few percent which is up to 100 % in case of pure SMPs. Finally, a balance between the filler content and filler type should be maintained to achieve better shape-memory properties for specific applications [07Sah].

9.4.3.2 Light-Sensitive SMP Nanocomposite

Light, another stimulus, can also be used to increase SMP temperatures above the transition temperature to impart shape recovery. Insertion of nano CBs and CNTs into the matrix of SMPUs enhances the heat absorption capacity of the SMPU nanocomposites, which leads to the development of an intravascular laser-activated therapeutic device [02Mai].

9.4.3.3 Magnetic-Sensitive SMP Nanocomposite

Magnetic-sensitive SMP nanocomposites can be prepared by addition of ferromagnetic fillers. Incorporation of nano iron(II,III) oxide nanoparticles into the thermoplastics and thermoset SMP matrix enables the remote actuation of SMP nanocomposites in a magnetic field. Addition of Ni-Zn ferrite particles generates indirect magnetic actuation into the thermoset polyurethane matrix. In comparison to conventional (shape recovery triggered by direct heating) shape-memory nanocomposites, magnetic-sensitive nanocomposites have several advantages which are as follows:

(a) Possibility of activation of more complex-shaped device due to consistent heating is expected to achieve for any kind of device geometry.
(b) Possibility of selective heating of specific device areas.
(c) Remote actuation results, the possibility of formation of embedded devices which can be actuated later by the application of an external magnetic field.
(d) Selection of a ferromagnetic material with a Curie temperature within the safe medical limits eliminates the danger of overheating.

Thus, magnetic-sensitive shape-memory nanocomposites have good potential biomedical applications also [06Sch].

9.4.3.4 Water-/Solvent-Sensitive SMP Nanocomposite

For a certain period of time, if SMPUs are exposed in a high humid environment or solution, its glass transition temperature (T_g) decreases because of the plasticizing effect of the water molecules on the polymeric materials and hence increase in the flexibility of the macromolecular chains. This effect leads to the shape recovery of the deformed SMPU. Water-driven shape recovery effect of CB/SMPU nanocomposite has been studied in detail and it reveals that CB/SMPU nanocomposite recovers most of its original shape from deformed shape after immersion in water for 2 h at room temperature. Although higher content of CB reduces the moisture sensitivity of the nanocomposites.

Addition of hydrophilic or water-soluble ingredients into SMP matrix phase is another way for development of moisture-/water-active SMP nanocomposites, like biodegradable water-soluble chitosan films cross-linked with an epoxy compound has been developed that can be used or drug delivery purpose [04Yan].

9.4.4 SMP Nanocomposites with Special Functions

9.4.4.1 SMP Nanocomposites with Electromagnetic Interference Shielding (EMISE)

Novel properties of CNT-reinforced SMPs have been studied by many scientists, and it have been explored into many potential applications. It has been found those

MWCNTs/SMPU nanocomposites are excellent shielding materials for electromagnetic interference. Electromagnetic interference shielding effectiveness (EMISE) of MWCNTs/SMPU nanocomposites is strongly influenced by vapor grown carbon fibers (VGCFs) content and the specimen thickness [07Zha].

9.4.4.2 SMP Nanocomposites with UV Protection

CNT-reinforced SMP nanocomposites show good UV protection properties as a consequence of the better UV-radiation absorption property of CNTs. Even cotton fabric with hydrophilic SMPU solution, which contains MWCNTs, shows excellent protection against UV radiation [02Bac].

9.4.4.3 SMP Nanocomposites with Smart Water-Vapor Permeability (WVP)

Microstructure of polyurethane has a strong influence on mass transport through the polyurethane membranes. It can be observed that high content of MWCNTs strongly increase the WVP of the polyurethane membrane. Improvement of WVP of the polyurethane membrane can be explained from two aspects. In one aspect, MWCNTs constrain the forming of ordered soft segment phase structure, and in other aspect, straight MWCNTs with large aspect ratio forms a relatively straight free pathway for the diffusion of water molecules on the surface of MWCNTs or inside MWCNTs to pass through [07Mon].

9.5 Conclusions

Generally, SMP nanocomposites exhibit novel performance properties which are distinctly different from the pure counterparts. As a result, SMP nanocomposites can be suitable for various applications. It can be anticipated that research in SMP nanocomposites will grow further due to the promising potential applications. Still there are some shortcomings. In some cases, too low recovery stress of SMP nanocomposites confine their applications in various stages. Shape recovery stress can be improved by the incorporation of other materials which results in the low shape recovery ratios and deformable strain of the SMP nanocomposites. On the other hand, some SMP nanocomposites become very soft above its switch temperature. Multistep or two-way SME is at its initial state only. Complicated SME with controllable recovery speed, exact recovery shape, and recovery level at different steps is much more preferred for complicated applications. Ultimately, most of the shape recovery of the SMP nanocomposites is triggered by temperature, which also implies limited applications of SMP nanocomposites. In future, further study is still needed for the development of multisensitive SMP nanocomposites that can respond to different parameters according to the applications.

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