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MATERIALS FOR POLYMER NANOCOMPOSITES

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1.1 INTRODUCTION

Nanotechnology is technology concerning processes that are relevant to physics, chemistry, and biology taking place at a length scale of 1 divided by 1000 million of a meter [1]. Nanotechnology is a fast growing field concentrated on the invention

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of functional materials, smart devices and systems by controlling matter on the nanometer scale and the exploitation of novel phenomena and properties at that length scale [2]. Nanotechnology is so important because it is relatively cheap, safe, and clean and the financial rewards are relatively very high [3]. Significant investments by industry, academia and government are being made with the hope that advances in nanotechnology will have an intense and positive effect on our lives [4].

Nanostructured materials are materials with a microstructure and the characteristic length scale of which is on the order of a few nanometers. They have attracted great interest in recent years because of the unusual mechanical, electrical and optical properties by the combination of bulk and surface properties with the overall behavior.

The field of nanotechnology obviously refers to polymer science and technology, which includes polymer-based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode, polymer-bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibers, imprint lithography, polymer blends, and nanocomposites. In the field of nanocomposites, polymer matrix-based nanocomposites have become a prominent area of current research and development in the field of nanotechnology [5]. Polymer nanocomposites are polymer matrix composites in which the fillers are less than 100 nm in at least one dimension. When incorporating fillers with polymers, the beneficial features of both can be combined. The beneficial features that can be contributed from the reinforcing filler include mechanical strength; chemical and thermal stability; and electrical, ferroelectric, magnetic, and diverse optical properties. Apart from their improved properties, these nanocomposite materials are also easily extruded or molded to near-final shape, simplifying their manufacturing. This lightweight advantage could have significant impact on environmental concerns and other potential benefits. From the beginning of polymer chemistry, the technique of incorporating microfillers into the polymer matrix is used. The quality of traditional composite materials is not comparable to recent nanocomposite materials because of the poor dispersion and poor interaction between microfiller and polymer matrix.

The interest in polymer nanocomposites has emerged for several reasons. First, nanoscale fillers often have properties that are different from the bulk properties of the same material [6]. Owing to the small size of nanofillers in comparison to microfillers, early failure can be prevented, leading to nanocomposites with enhanced ductility and toughness [7, 8]. It has also been shown that nanoparticles can increase the electrical breakdown strength [9] and have small optical scattering defects [10] due to their small size. Owing to the large surface area of the fillers, nanocomposites have a large volume of interfacial matrix material with properties different from the bulk polymer [11, 12].

This chapter focuses on the materials for the polymer nanocomposite in detail. The state of the art, new challenges, and opportunities in the area of polymer nanocomposite systems will be discussed in this chapter. The recent developments in the area of polymer nanocomposites will be highlighted. The various unresolved issues and new challenges in polymer nanocomposites will also be discussed.

1.2 NANOCOMPOSITE FRAMEWORK

The composite is a material that is formed from two or more components according to the end application and desired properties. The first component is called the matrix, which can be metallic, polymeric, or ceramic. It controls the major properties of the composite, holds the filler materials, protects fillers from the surrounding environment and transfers load to the fillers. The second component is the reinforcement material, which is usually added in small amounts compared to the weight of the whole mixture. Reinforcement can be of different forms such as particles, fibers, filler, flake, and lamina. The properties of the composite are closely related to concentration; distribution; orientation; and the nature, size, and shape of reinforcements [13].

1.2.1 Nanoscale Fillers

By scaling the particle size down to the nanometer scale, it has been shown that novel material properties can be obtained. Nanoparticles are materials of two or more dimensions, with size in the range of 1–100 nm. Nanoparticles show unique size-dependent physical and chemical properties: the chemical composition and the shape of a nanoparticle also influence its specific properties. Nanoparticles can thus be classified based on dimension, source, chemical nature, size, shape, and so on. However, one interesting classification can be based on the dimension. The fillers can be classified into three groups depending on their shape. They are 1D nanofillers such as nanorods, fibers, or tubes with varying aspect ratios; 2D fillers such as platelets with a thickness of the lower nanometer range and the dimensions in length and width far exceed the particle thickness; 3D nanoparticles, which are spherical in shape (Fig. 1.1).

1.2.1.1 Zero-Dimensional Nanofillers Silsesquioxanes are nanostructures having the empirical formula $\text{RSiO}_{1.5}$, where R is a hydrogen atom or an organic functional group such as an alkyl, alkylene, acrylate, hydroxyl, or epoxide unit [14]. Polyhedral oligomeric silsesquioxane (POSS) is a true hybrid inorganic/organic chemical composite that possesses an inner inorganic silicon and oxygen core $(\text{SiO}_{1.5})_n$ and external

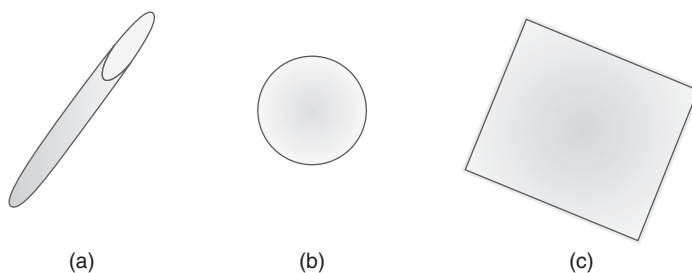


Figure 1.1 Classification of nanoscale fillers: (a–c) 1D, 2D, and 3D nanomaterials.

organic substituents that can feature a range of polar or nonpolar functional groups. POSS nanostructures have diameters ranging from 1 to 3 nm [15]. The incorporation of POSS moieties into a polymeric material can dramatically improve its mechanical properties (e.g., strength, modulus, rigidity) as well as reduce its flammability, heat evolution, and viscosity during processing. These enhancements can apply to a wide range of applications such as commercial thermoplastic polymers, high-performance thermoplastic polymers, and thermosetting polymers [16, 17]. Both monofunctional and multifunctional monomers of these types have been used to prepare commercial and/or high-performance thermoplastic polymers [18–20] and thermosetting polymers [21, 22]. Properties of POSS-containing polymer composites depend on the successful incorporation of POSS particles into polymeric matrices. Two approaches have been adopted to incorporate POSS particles into polymer matrices: (i) chemical cross-linking and (ii) physical blending (Fig. 1.2).

Semiconductor nanocrystals especially have generated a lot of interest among researchers in the past decades due to their wide range of applications in photonics, electronics, and optoelectronics [23, 24]. For the fabrication of devices, quantum dots (QDs) have to be well dispersed and must be compatible with the supporting matrix while transferring it into a composite [25–27]. Polymers are found to be the ideal candidate for the same. These multicomponent materials usually possess the combined novel properties of both the nanoparticles and the polymer matrix [28, 29]. Due to the organophobic surface of the QDs, they tend to agglomerate inside the polymer matrix, so surface functionalization of QDs may be needed to enhance the dispersion of filler in the polymer matrix [30].

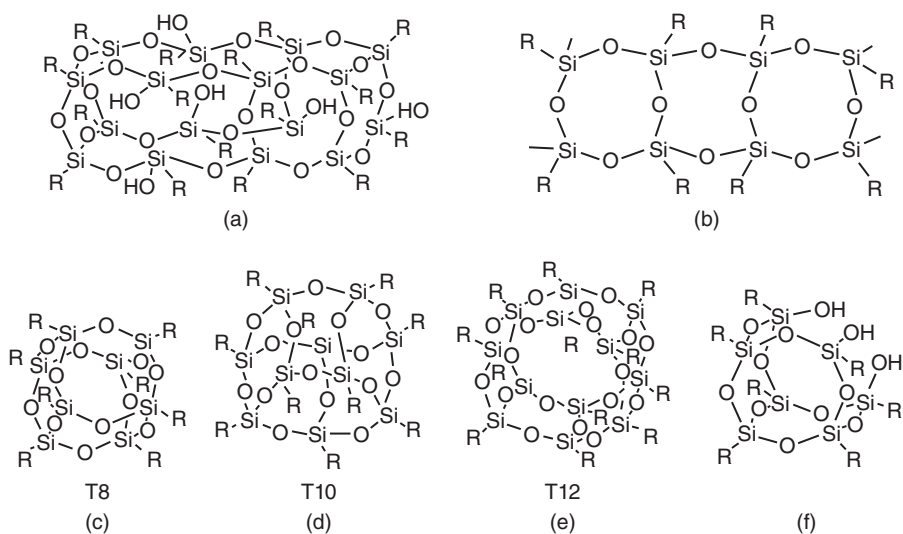


Figure 1.2 Structures of silsesquioxanes [14]: (a) random structure, (b) ladder structure, (c–e) cage structures, and (d) partial cage structure.

1.2.1.2 One-Dimensional Nanofillers One-dimensional nanofillers are nanorods, fibers, or tubes with varying aspect ratios. Rod like nanoparticles can impart anisotropic properties to composite materials. Carbon fiber reinforced polymer matrix composites form a special class of high-performance materials, which has received huge research attention in the past several decades because of the unique combination of properties such as lightweight, higher specific strength, stiffness, rigidity, corrosion, and environmental resistance. They are synthesized from the pyrolysis of hydrocarbons or carbon monoxide in the gaseous state in the presence of a catalyst [31, 32]. Nanocarbon fibers have typical dimensions with an outer diameter of 50–200 nm, inner diameter of 30–90 nm, and length in the range of 50–100 μm . Carbon nanofibers (CNFs) are known to have wide-ranging morphologies from a disordered bamboo-like structure [33] to highly graphitized “cup-stacked” [34] structures where the conical shells of the nanofiber are nested within each other. Vapor-grown CNFs have been used to reinforce a variety of polymers, including elastomers [35, 36], thermoplastics such as polypropylene (PP) [37–40], polycarbonate [41, 42], nylon [43], and thermosets such as epoxy (Fig. 1.3) [45, 46].

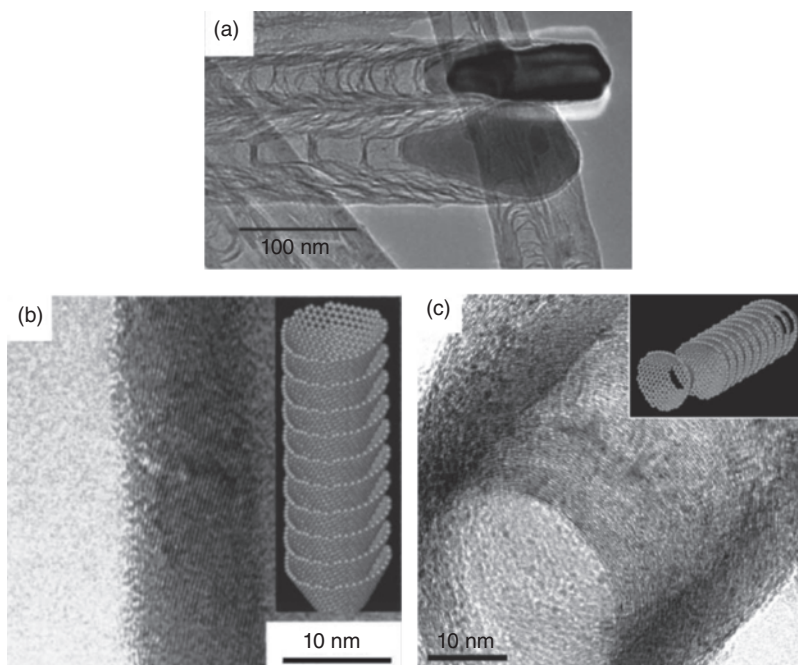


Figure 1.3 TEM images of the nanoscale structure of carbon nanofibers showing (a) disordered bamboo-like structures, reproduced from Merkulov et al. [33] with permission of AIP Publishing; (b) highly graphitized sidewall of a cup-stacked nanofibers showing the shell tilt angle, reproduced from Endo et al. [34] with permission of AIP Publishing; and (c) a nesting of the stacked layers (insets: molecular models), reproduced from Endo et al. [44] with permission of AIP Publishing.

However, the literature about nanocomposites with nanorods mainly comprises the huge and promising field of carbon nanotube (CNT) composites. Since their discovery by Iijima [47], they have attracted very much and are now being used for many fundamental and advanced applications. CNTs, basically consisting of sheets of graphite rolled up into thin cylinders, with Young's modulus of about 1 TPa and tensile strength up to 63 GPa are considered to be ideal reinforcement materials. Multiwalled nanotube (MWNT) comprises a number of graphene layers coaxially rolled together to form a cylindrical tube. Each carbon atom within the atomic layer of a graphene sheet is covalently bonded to three neighboring carbon atoms. Three sp^2 orbitals on each carbon form σ -bonds with three other carbon atoms. One $2p$ orbital remains unhybridized on each carbon; these orbitals perpendicular to the plane of the carbon ring combine to form the π -bonds. The atomic interactions between the neighboring layers are the van der Waals forces [48]. The outer diameter of MWNTs is about 3–10 nm. The outstanding thermal and electric properties, combined with their high specific stiffness and strength, and very large aspect ratios have stimulated the development of nanotube-reinforced composites for both structural and functional applications [49]. The first polymer nanocomposites using CNTs as a filler were reported in 1994 by Ajayan et al [50]. Introducing CNTs to polymer matrices modifies mechanical [51], electrical [52], thermal [53], and morphological properties [54] of the produced nanocomposite (Fig. 1.4).

Although CNTs have excellent properties, major challenges faced during the incorporation of nanofillers include their processing difficulty and tendency to form agglomerates [56, 57]. The fine dispersion of nanofillers in polymer has been still the most challenging task for their practical applications. Several strategies have been developed for the better dispersion of fillers in the polymer matrix, which includes

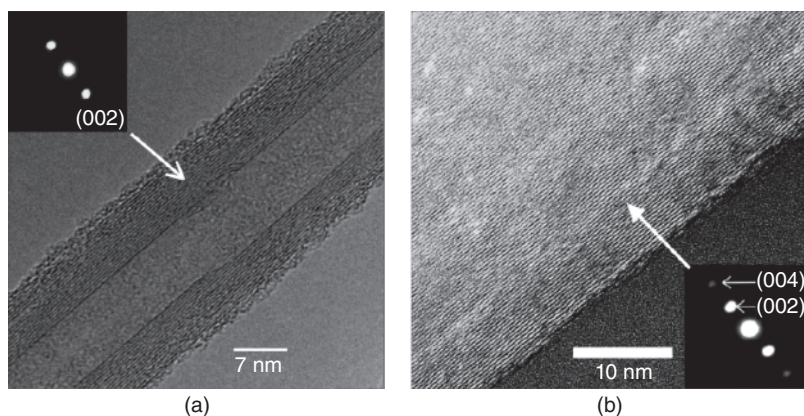


Figure 1.4 HRTEM images of MWNTs: (a) 18-nm-diameter nanotube produced at 675 °C and (b) 180-nm-diameter nanotube produced at 775 °C. The insets are the corresponding nanodiffraction patterns showing both tubes well graphitized at low synthesis temperatures. Reproduced from Andrews et al. [55] with permission of American Chemical Society.

covalent and noncovalent functionalization of CNT [58]. The nanotube–polymer interaction is believed to play an important role in determining the overall properties of the nanocomposites. Several studies have been reported based on surface-modified CNT polymer nanocomposites [59–61].

The halloysite nanotubes (HNTs) is a kind of alumina silicate clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$ with 1:1 layer) having hollow micro- and nanotubular structure. It has been reported that HNTs have typical dimensions of 10–50 nm in the outer diameter and 5–20 nm in the inner diameter with 2–40 nm length [62, 63]. HNTs have high mechanical strength and modulus, and these features make it an ideal candidate for reinforcement in polymer nanocomposites. So many varieties of biological and nonbiological applications are recommended for HNT-based polymer nanocomposites [64].

1.2.1.3 Two-Dimensional Nanofillers Two-dimensional fillers are platelets with thickness of lower nanometer range and the dimensions in length and width far exceed the particle thickness. Typical fillers used in polymer nanocomposites (PNCs) as platelets include layered silicates or layered double hydroxides (LDHs) such as graphene. The average interparticle spacing between layers depends on the extent of intercalation and mineral concentration, generally the higher the mineral concentration the smaller the spacing.

The clay known as montmorillonite (MMT) consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers [65]. The single layers have a planar structure with a thickness of about 1 nm and usually a length of several hundred nanometers. Due to the isomorphic substitution of Al^{3+} into the silicate layers or Mg^{2+} for Al^{3+} , the layers bear negative surface charges being compensated by inorganic cations adsorbed in the interlayer space. Because of their hydrophilic surface, natural layered silicates show poor miscibility with polymers. Thus, for the preparation of clay nanocomposites, the layers have to be separated from each other via ion exchange of the inorganic cations with organic cations such as alkylammonium ions [66].

Among the layered silicates, MMT is commonly used as reinforcement for the polymer–clay because it is an environmentally friendly material, which is readily available in large quantities with relatively low cost, and its intercalation chemistry is well understood. The use of organoclays as precursors to nanocomposite formation has been extended into various polymer systems including epoxys, polyurethanes, polyimides, nitrile rubber, polyesters, polypropylene, polystyrene (PS), and polysiloxanes [67–69]. In phase separated nanocomposites the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. Intercalated structures are self-assembled, well-ordered multilayered structures where the extended polymer chains are inserted into the gallery space of the clays. This leads to an expansion of the interlayer spacing. In an exfoliated structure, individual silicate sheets lose their layered geometry as a result of delamination and are dispersed as nanoscale platelets in a polymer matrix [70].

LDHs form a typical class of layered minerals that are frequently termed anionic clay minerals. LDHs can be of both natural origin and synthetically prepared in the laboratory. The general chemical formula for LDHs is $[M^{II}_{1-x}M^{III}(\text{OH})_2]^{x+}(A^{n-})_{x/n} \cdot y\text{H}_2\text{O}$, where M^{II} represents a divalent metal ion, for example, Mg^{2+} , Ca^{2+} , Zn^{2+} , and so on; M^{III} represents a trivalent metal ion, for example, Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , and so on; and A^{n-} represents an anion, for example, Cl^- , CO_3^{2-} , NO_3^- , and so on. The anions remain in the interlayer region. The synthesis of nanosized LDH platelets can be generally classified into two approaches: “bottom-up” and “top-down.” To date, the “top-down” synthesis is the most widely developed method. The delamination and reconstruction method is another promising technique for synthesizing organomodified LDHs. One can obtain exfoliated LDH layers by this method, which subsequently aid in the dispersion of these layers into polymers. Since the charge density of LDH is very high, it requires the modification of the LDH interlamellar environment and then selection of an appropriate solvent system, for example, ion-exchange intercalation of the LDH with anionic surfactant such as dodecyl sulfate (DDS). Delamination/exfoliation then occurs when it is dispersed in a highly polar solvent, which is able to solvate the hydrophobic tails of the intercalated anions (Fig. 1.5) [72].

The modification of LDH materials is almost a requirement prior to the fabrication of elastomer composites because this process facilitates the intercalation of the elastomer chains, resulting in enhanced properties. The basic goal of the organic modification process is to increase the interlayer spacing of LDH materials to make the intercalation of large species, such as polymer chains and chain segments, easier. It is believed that the anionic organic surfactants that have at least one anionic end group and a long hydrophobic tail are the best materials for serving the desired purpose [73]. Although there are many possible strategies to synthesize exfoliated polymer/LDH nanocomposites, generally the methods can be classified into three principal options: (i) intercalation of the monomer molecules and in situ polymerization, (ii) direct intercalation of extended polymer chains, (iii) pre-exfoliation and followed by mixing with polymer, as shown in Figure 1.6a [74]. The use of modified LDHs with elastomers substantially improves their mechanical, thermal, and optical properties. Even “smart properties” of elastomers, such as reversible thermotropic optical characteristics, have been realized with the use of LDH-based multifunctional additives in rubber formulations [75].

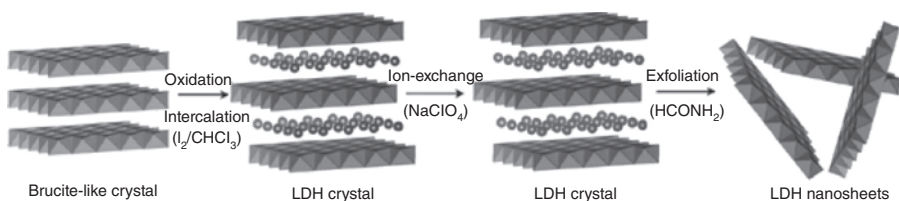


Figure 1.5 Schematic illustration of topochemical synthesis and exfoliation of Co^{2+} - Fe^{3+} LDH. Reproduced from Renzhi et al. [71] with permission of American Chemical Society.

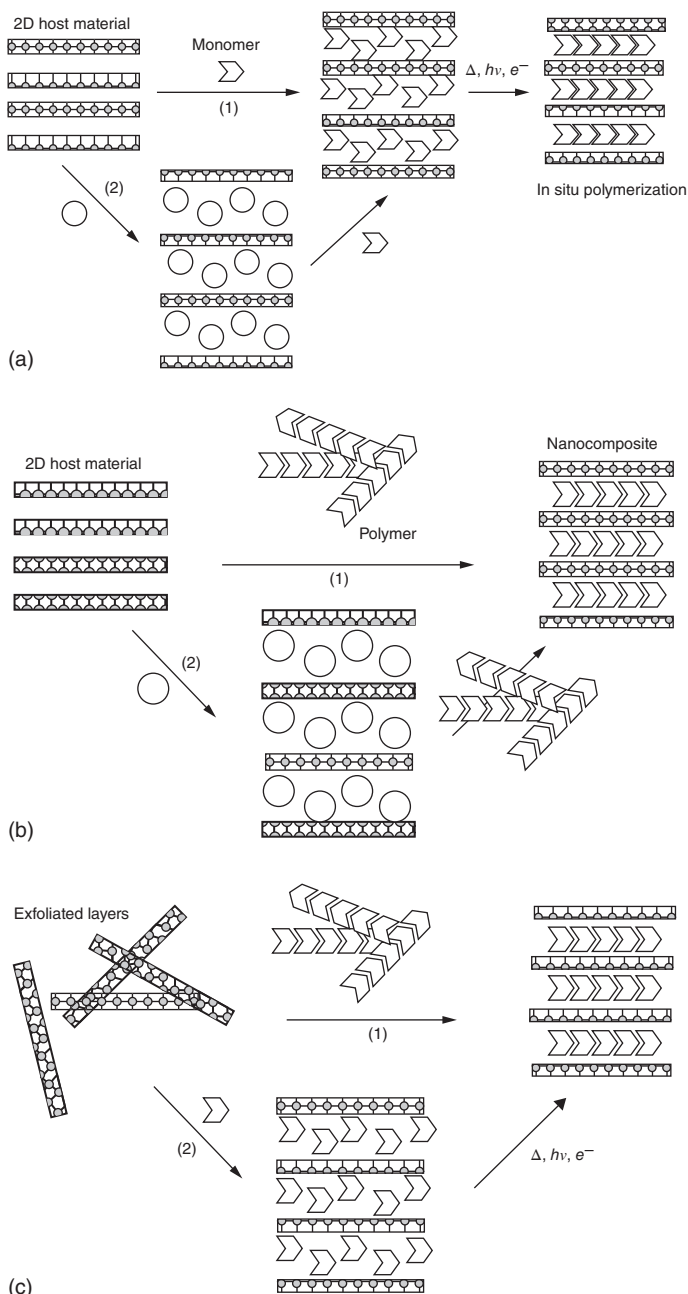


Figure 1.6 Pathway of nanocomposite preparation by (a) monomer exchange and in situ polymerization, (b) direct polymer exchange, and (c) restacking of the exfoliated layers over the polymer. Reproduced from Leroux and Besse [74] with permission of American Chemical Society.

Natural flake graphite (NFG) is the polycrystalline form of carbon comprising layered planes containing hexagonal arrays of carbon atoms to form an atomically flat-stacked material in three dimensions. Covalent bonds bind the carbon atoms in the same plane together with van der Waals forces between successive layers separated by 0.337 nm. Because of the very weak van der Waals forces, it is quite easy for small atoms, ions, and molecules to intercalate between the layers to form expanded graphite (EG) [76], graphite nanoplatelets (GNPs) [77], and graphene [78]. Expanded graphite (EG), a form of graphite intercalation compound (GIC), is fabricated from NFG through chemical or thermal expansion [79]. Nanosheets or platelets (GNPs) have proved their significance as strong, versatile, and inexpensive fillers in composite materials [80]. A schematic representation showing all kinds of graphitic derivatives and their interdependence is given in Figure 1.6a–c.

Since its discovery by Geim and Novoselov [81] and Novoselov et al. [82] in 2004, graphene has attracted in both academia and industry because it is one-atom thick and consists of sp^2 carbon atoms arranged in a honeycomb lattice structure leading to exceptional in-plane functional and mechanical properties. The major fabrication methods of graphene include micromechanical cleavage [83]; chemical vapor deposition (CVD) [84]; and the oxidation, exfoliation, and reduction of graphite [85]. Two-dimensional graphene is an allotrope of carbon in which each carbon atom is bonded with another carbon by sp^2 bonds. Here, carbon atoms are densely packed in a honeycomb crystal lattice with a bond length of 0.141 nm. Density of graphene is around 0.77 gm/cm^3 , and a single-layered graphene is predicted to have a large surface area close to $2600 \text{ m}^2 \text{ gm}$. The important properties of graphene are given in Figure 1.7.

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 [86, 87]. The functional groups attached to graphene can be small molecules or polymer chains, and this can be performed using chemical methods [88–90]. Polymer–graphene nanocomposites show not only improved mechanical properties but also impressive functional properties, such as electrical (semi-)conductivity, unique photonic/optical transportation, anisotropic transport, low permeability, and fluorescence quenching [91, 92]. A thorough investigation of the properties of various graphitic fillers, such as NFG, expanded graphite (EG), GNP, and graphene, is undertaken by various researchers [93].

1.2.1.4 Three-Dimensional Nanofillers Fullerenes pertain to the carbon molecules of C_{28} , C_{32} , C_{44} , C_{50} , C_{58} , C_{60} , C_{70} , C_{72} , C_{78} , C_{80} , and C_{82} [94]. They have many interesting properties, such as high surface area, porosity, thermal stability, nontoxicity, biocompatibility, and hydrophilic functionalization. Many of the polymer scientists tried to use this molecule as a building block to construct novel materials with unusual properties. Fullerene C_{60} and its polymeric composites have been demonstrated to possess interesting optoelectronic properties, photovoltaic, and optical limiting applications [95].

Carbon black, the amorphous form of carbon, is primarily used as commercial filler/additive of ultraviolet (UV) light stabilizer, antioxidant and antistatic agent in

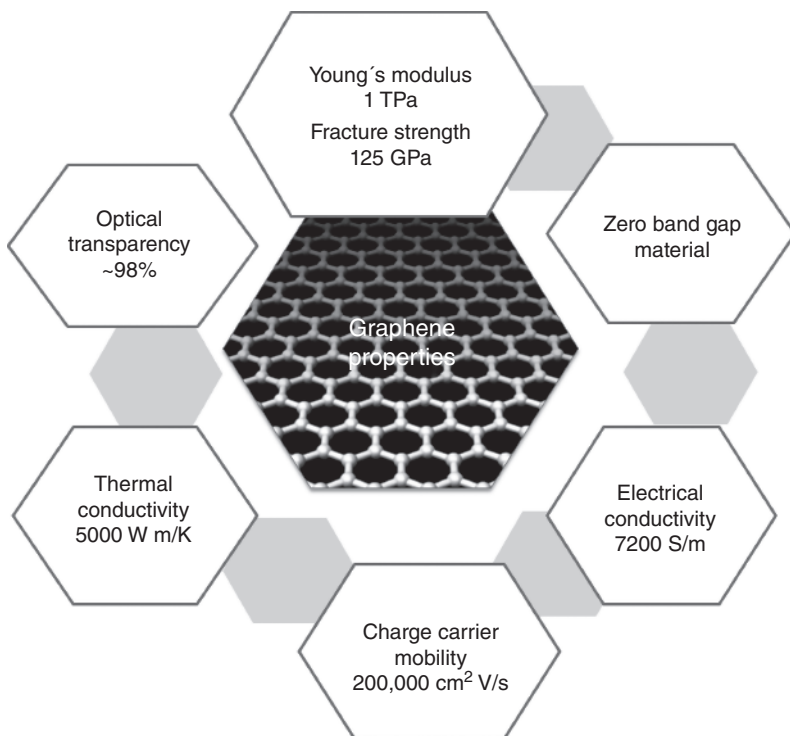


Figure 1.7 Properties of graphene.

rubber industry, pigment or colorant in dye industry, conductive filler in polymer, and composite industry for semiconductive applications [96]. Carbon black has become one of the most widely used reinforcements in engineering applications of polymer-based composites due to its high temperature tolerance, elastic modulus and tensile strength, low weight, and thermal expansion [97]. Both high surface area and high degrees of porosity are the critical characteristics of carbon black that impart improvement in the overall performance at lower loadings in polymer composites [98–101].

1.2.1.5 Metal Oxides Polymer nanocomposites containing surface-engineered metal oxide continuously offer new opportunities to enhance desired properties or functionalities such as optical transparency, ductility, flexibility, or molecular mobility [102, 103]. In order to prevent the agglomeration of these inorganic metal oxides in organic polymer matrix, various kinds of functional methods are adopted that include the use of surfactants [104] and silane coupling agents [105]. Polymer matrices reinforced with modified inorganic nanoparticles combine the functionalities of polymer matrices, which include low weight and easy formability with the unique features of the inorganic nanoparticles. The nanocomposites obtained by

incorporation of these types of materials can lead to improvements in several areas such as optical, mechanical, electrical, magnetic, rheological, and fire retardant properties [106, 107].

Development of ceramic nanoparticles with improved properties has been studied with much success in several areas such as synthesis and surface science. Examples of ceramics are silica, alumina, titania, zirconia, silicon nitride, silicon carbide, and so on. Nanosized silica, SiO_2 , has been widely used as filler in engineering composite. Some of the widely used methods to synthesize silica nanoparticles are sol-gel process, reverse microemulsion, and flame synthesis. The sol-gel process is widely used to produce pure silica particles due to its ability to control the particle size, size distribution, and morphology through systematic monitoring of reaction parameters.

The chemical modification of silica surface with organofunctional groups is an important step toward the preparation of silica-polymer nanocomposites. More precisely, the surface modifications have been reported to enhance the affinity between the organic and inorganic phases and at the same time improve the dispersion of silica nanoparticles within the polymer matrix. Surface modification of silica nanoparticles can be carried out by using various types of silane coupling agents. Surface modification makes the possibility to graft or conjugate the nanostructured silica with polymers or proteins for future applications in biotechnology and medicine such as dental filling composites, cancer treatment, and drug delivery

ZnO is an inorganic filler and a semiconductor material existing in a diversity of structures. It is extensively used due to its distinctive optical, electrical, photocatalytic, optoelectronic, antibacterial, and dermatological properties [108, 109] Iron oxide (Fe_2O_3), the most common oxide of iron, has important magnetic properties and is a convenient compound for the general study of polymorphism and the magnetic and structural phase transitions of nanoparticles. The existence of amorphous Fe_2O_3 and four polymorphs (α , β , γ , and ϵ) is well established [110, 111]. Zirconium dioxide possesses excellent properties, namely high strength, high fracture toughness, excellent wear resistance, high hardness, and excellent chemical resistance. Hence, ZrO_2 nanoparticles appear as an attractive option to be used as reinforcement of polymers, in order to produce composites with enhanced performance [112].

TiO_2 is an example for inorganic filler. It has so many interesting properties making it a versatile one. Titanium dioxide is an inexpensive, nontoxic, and photostable inorganic material, which has good optical and photocatalytic properties for many applications [113]. Due to its high refractive index and ability to reflect and refract or scatter light more effectively than any other pigment, titanium dioxide has for many years served and is still serving as a white pigment. It is also used to provide protection against UV effect because it is capable of absorbing UV light.

Al_2O_3 nanoparticles can be prepared by flame spray pyrolysis, reverse microemulsion, sol-gel, precipitation, and freeze drying [114, 115]. It has excellent optical, transport, mechanical, and fracture properties [116, 117]. It has applications in various fields such as wastewater and soil treatment by the removal of heavy metal ions and antimicrobial applications, ceramic ultrafilters and membranes to remove pathogenic microorganisms, for gas separation, in catalysis and absorption processes and drug delivery [118, 119].

1.2.2 Choice of Polymeric Matrices

By taking the benefits of infinite number of monomers, oligomers, and chemicals available, we can tune the properties of matrices based on our desired application. Properties that can be tuned or controlled include controlled hydrophobicity, ionizability, crystallinity, transparency, toughness, strength, densities, conductivity, and degradability [83, 120]. Polymers are giant molecules with molar mass ranging from several thousands to several millions and are composed of a large number of smaller parts joined together through chemical bonds. This era can be called as polymer age since polymer can be used for the production of various things, which includes plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tires, gears and seals, electrical insulating materials, and machine parts, which has completely revolutionized the daily life as well as the industrial scenario. The word polymer is derived from Greek words *poly* meaning many and *mers* meaning parts or units of high molecular mass, each molecule of which consists of a very large number of single structural units joined together in a regular manner. The reaction by which the monomers combine to form a polymer is known as polymerization [121]. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything such as water, heat, or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

1.2.2.1 Classification of Polymers Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless forms and numbers because of very large number and type of atoms present in their molecule [122]. Polymer is the most widely used matrix material in composites. Polymers are lighter in weight, softer, and easier to be shaped than metals or ceramics. Polymers themselves are soft and have low strength, low electrical conductivity, and low thermal stability. Owing to their lighter weight and ease of manufacturing, polymers have many industrial applications (Fig. 1.8). Polymers can be generally classified based on the following:

- 1) Their origin – natural and synthetic
- 2) Their structure
- 3) Molecular forces
- 4) Polymerization reaction
- 5) Their steric structure

1.2.2.1.1 Classification Based on Source There are three subcategories in this type of classification. (i) Natural polymers: These polymers are found in nature such as in plants and animals. Examples are proteins, cellulose, starch, resins, and rubber. (ii) Semisynthetic polymers: These polymers are obtained by simple chemical treatment of natural polymers to change their physical properties, for example, starch and silicones. (iii) Synthetic polymers: The fibers obtained by the polymerization of simple chemical molecules in laboratory are synthetic polymers, for example,

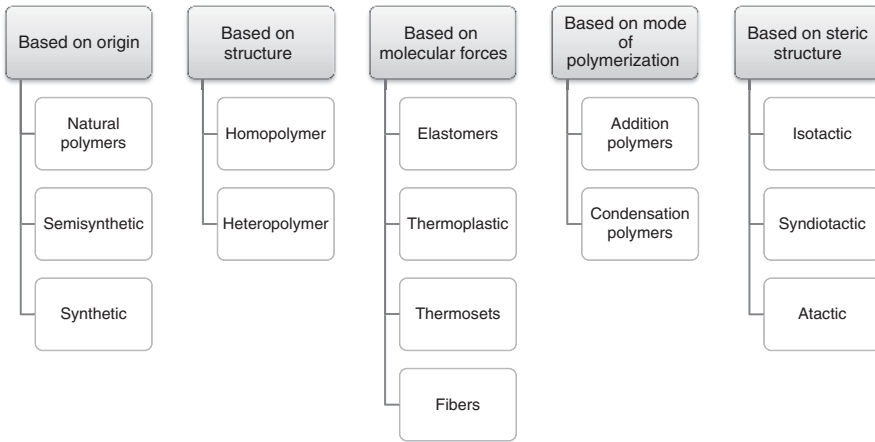


Figure 1.8 Classification of polymers.

nylon, polyethene, polystyrene, synthetic rubber, polyvinyl chloride (PVC), Teflon, and so on.

1.2.2.1.2 Classification Based on Structure Polymers that are formed from single monomers are referred to as homopolymers and are produced from two or more monomers called heteropolymers or copolymers. Many of the well-known polymers are homopolymers such as polyethylene, polypropylene, and PVC; polymethyl methacrylate (PMMA); polystyrene; polytetrafluoroethylene (PTFE); and poly acrylonitrile. There are several types of copolymers that include alternating copolymer, random copolymer, block copolymer, and graft copolymer.

1.2.2.1.3 Classification Based on Molecular Forces Mechanical properties of polymers such as tensile strength, toughness, and elasticity depend on intermolecular forces such as van der waals forces and hydrogen bonding. On the basis of these forces, they are classified as elastomers, fibers, thermoplastics, and thermosetting polymers.

An elastomer is a polymer with viscoelasticity (having both viscosity and elasticity) and very weak intermolecular forces, generally having low Young's modulus and high failure strain compared with other materials [123]. They are flexible or "rubbery" materials that can readily be deformed and return rapidly to almost their original shape and size once released from stress, thus making them able to form reliable seals. A few "cross-links" are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanized rubber. Natural and synthetic rubbers are common examples of elastomers.

Fibers are the thread-forming solids that possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces such as hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. They have much lower elasticity compared to

plastics and elastomers, for example, polyamides (nylon 6,6), polyesters (terylene), and so on.

A thermoplastic or thermosoftening plastic is a plastic material, typically a polymer that becomes flexible or moldable above a specific temperature and solidifies upon cooling [124]. In contrast to elastomers, plastics have a greater stiffness and lack reversible elasticity.

Thermosetting polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross-linking of the polymer chain molecules, thus producing giant molecules such as phenolic resins, urea, epoxy resins, and diene rubbers.

1.2.2.1.4 Based on Polymerization Reaction Chain-growth polymerization (or addition polymerization) involves the linking of molecules having double or triple carbon-carbon bonds. Unsaturated monomers that have extra internal bonds are able to break and link up with other monomers to form a repeating chain. Chain-growth polymerization is involved in the manufacture of polymers such as polyethylene, polypropylene, PVC, PMMA, PS, PTFE, polyacrylonitrile, and so on. Different forms of chain-growth polymerization include free radical polymerization, cationic addition polymerization, anionic addition polymerization, and coordination polymerization reactions.

Step-reaction (condensation) polymerization is another type of polymerization. This polymerization method typically produces polymers of lower molecular weight than chain reactions and requires higher temperatures to occur. Stepwise reactions involve two different types of difunctional monomers that react with one another forming a chain. In this reaction, some of the atoms of the monomer are split off in the reaction as water, alcohol, ammonia, or carbon dioxide. Examples for condensation polymers are polyesters, polyamides, phenol-methanal plastics, polyurethanes, and so on.

1.2.2.1.5 Based on Steric Structure Another method of classifying polymers is by examining their steric structure. Polymers with side chains can be divided into two classes: one (stereoregular) that has a recurring pattern in terms of stereochemistry and the other (atactic) with no regular structure. Isotactic polymer: It is a type of polymer in which the characteristic groups are arranged in the same side of the main chain. A polymer is said to be syndiotactic if the characteristic groups are arranged in an alternate manner and it is called atactic if the characteristic groups are arranged in a random manner around the main chain.

The scientific and commercial progress in the area of polymer blends during the past decades was tremendous and was driven by the realization that by blending, new materials can be developed and can be implemented more rapidly and economically [125]. Interpenetrating polymer network (IPN) refers to multicomponent materials consisting of two or more cross-linked networks in which at least one is cross-linked in the presence of another [126]. IPN is emerging as a promising matrix to reinforce nanofillers [127]. Dendrimers are molecules with globular structure in

which well-defined branches radiate from a central core, becoming more branched and crowded as they move to periphery. These types of polymers have received considerable interest with applications that includes drug delivery agents, micelle mimics, and so on [128, 129].

1.3 RECENT DEVELOPMENTS AND OPPORTUNITIES IN THE AREA OF POLYMER NANOCOMPOSITES

Polymer nanocomposites containing organic and inorganic nanofillers have attracted extensive interest from academic and industrial perspectives due to the unique characteristics of nanoparticles, including their large surface area, high surface reactivity, and relatively low cost. The POSS nanocomposites are composite materials reinforced with silica cages, ultrafine fillers of nanometer size, almost equal to the size of the polymer matrix. Several high-performance POSS nanocomposites can be used as light-emitting diodes, liquid crystals, photoresist materials, low dielectric constant materials, self-assembled block copolymers, and nanoparticles. QD-based polymer nanocomposites can be used to fabricate solar cells such as light-emitting diodes. By combining the excellent properties such as mechanical, electrical, and thermal properties of CNTs with polymers renders a vast range of potential applications. Large number of studies have been done to use these properties for industrial applications such as energy storage devices, electronics, sporting goods, automobiles, filters, sensors, and so on. Due to heat absorbing capability, these nanocomposites can be used in aerospace industries as electromagnetic wave absorption materials [130]. Reinforcement of CNTs into epoxy could improve the mechanical properties such as strength, stiffness, and durability of materials that could be used for further industrial applications as sports goods, such as badminton rackets, golf and hockey sticks, and ski poles. CNT/polymer nanocomposites also play very significant role in automobile engineering. Polymer nanocomposites reinforced with HNTs possess highly increased tensile and flexural strength, elastic moduli, and improved toughness. HNT/polymer nanocomposites also exhibit elevated thermal resistance, flame retardancy, and unique crystallization behavior [131]. Due to the tubular microstructure and the biocompatibility of HNTs, nanocomposites of HNT/polymer have demonstrated good drug encapsulation and sustained release abilities, gaining them extensive use as tissue engineering scaffolds and drug carriers [132, 133]. Other than biomedical applications, HNTs have potential applications in high-performance composites for aircraft/automobile industries and environmental protection. Graphene-based PNCs represent one of the most technologically promising developments to emerge from the interface of graphene-based materials and polymer materials. Conductive graphene-based PNCs can find applications in various fields such as field effect transistors [134], solar cells (and other optoelectronic applications) [135], energy storage devices [136], and electromagnetic wave interference shielding and antistatic coatings [137]. The mechanical reinforcement achieved at low loadings of graphene offers potential uses in weight-sensitive aerospace and automotive applications, and improved barrier

properties of graphene-filled composites suggest their use in packaging applications. An emerging research direction for graphene-based composites is focused on biomedical applications [138, 139]. Since the polymer/silica nanocomposites can not only improve the physical properties such as the mechanical properties and thermal properties of the materials but also exhibit some unique properties, which have attracted very much in many industries. Apart from common plastics and rubber reinforcement, many other potential and practical applications of this type of nanocomposite have been reported: coatings [140, 141], flame-retardant materials [142], optical devices [143, 144], electronics and optical packaging materials [145], photoresist materials [146], pervaporation membrane [146], ultrapermeable reverse-selective membranes, proton exchange membranes, and sensors [147, 148]. The incorporation of metal oxide nanofillers into organic matrices provides superior mechanical, optical, electronic, and thermal properties for the resulting organic-inorganic nanocomposite materials [149].

1.4 CHALLENGES IN THE AREA OF POLYMER NANOCOMPOSITES

Polymer nanocomposites are the excellent materials that find various applications in our daily life. There is still a considerable uncertainty in theoretical modeling and experimental characterization of the nanoscale reinforcement materials, particularly nanotubes. Then, there is a lack of understanding of the interfacial bonding between the reinforcements and the matrix material from both analytical and experimental viewpoints. The improvement in properties and applications of these composites will depend on how effectively we can handle the challenges. Some key challenges are as follows:

- The cost of nanoparticles and their availability are the challenges that remain to achieve good dispersion that pose significant obstacles to obtain improved properties to the nanocomposite materials.
- The critical challenges lie in how to prepare structure-controllable nanomaterial with high purity, geometrical identity, and consistently dependable high performance and how to break up nanomaterial products to obtain isolated nanoparticles.
- The next immediate challenge relates to the composite processing. The full exploitation of nanofiller-based nanocomposites will be determined both by the level of filler dispersion and alignment and by the cost-effective manufacturing of the final material, then how to enhance load transfer from a matrix to filler reinforcement, and so on. Proper dispersion as well as good compatibility between filler and polymer is the main factor that controls the properties.
- Among the many challenges as PNCs move beyond commodity plastic applications, precise morphology control is paramount [149]. Random arrangements of nanoparticles will not provide optimized electrical, thermal, or optical performance for many potential high-technology applications, such

as dielectric for electronic packaging, printed flexible electronics, engineered aerospace structural components, reconfigurable conductive adhesives, and optical gratings to just mention a few.

- Most applications of nanocomposites with the exception of packaging materials are intended for long-term and/or outdoor use. It is well documented that inorganic fillers often experimentally show a negative effect on the oxidative stability of the polymer independent of the structure, however, to a varying extent [150]. To moderate the negative influence of fillers on the (photo)oxidative stability, blocking of the active sites on the filler by the so-called filler deactivators or coupling agents is a potential solution. Through adjustment of the stabilizer composition and loading, it is possible to achieve protection of the polymer nanocomposite against oxidation and photooxidation to an extent as known from unfilled polymers and needed for the individual application [151, 152].
- One of the challenges in developing PNCs for advanced technology applications is a limited ability to predict the properties. Although the techniques exist to tailor the surface chemistry and structure of nanoparticle surfaces [153, 154], the impact of the nanoscale filler surface on the morphology, dynamics, and properties of the surrounding polymer chains cannot be quantitatively predicted.
- Other challenges include predicting the impact of heterogeneous filler distribution and filler geometries (e.g., wavy fibers). There are still many unresolved issues that need to be addressed theoretically and experimentally to harness the maximum benefits from nanomaterials in polymer composite systems.
- With the development of nanomaterials, the safety of nanomaterial is of special importance and the health hazards caused by many of these smart materials are of still unclear. It is generally agreed that small size means easy access to living organisms via inhalation or transdermally, and this may lead to an increased risk to living organisms.

1.5 RELATIONSHIPS OF MACROSCOPIC RHEOLOGICAL PROPERTIES TO NANOSCALE STRUCTURAL VARIABLES

A direct consequence of incorporation of fillers in molten polymers is a significant change in their steady shear viscosity behavior and the viscoelastic properties [155, 156]. Owing to the possibility to achieve thermodynamic equilibrium conditions, measurements of composition and condition dependencies of viscoelastic properties in the molten state are generally useful for theoretical prediction of the structure–property relationships in composite materials. As the filler nanostructure, the interparticle and polymer–filler interactions can all strongly influence both linear and nonlinear viscoelastic behavior; rheology appears to be a suitable technique to obtain reliable experimental data on polymer nanocomposites. Rheological experiments can be used to probe the properties of the interfacial region more precisely. The loss modulus is sensitive to the distribution of relaxation times (relaxation spectra) of the polymer matrix. When nanofiller is added, the mobility of

the polymer chains is altered and the relaxation spectra can either shift or broaden. Thus, rheology has been used in nanoscale composites to probe the extent, structure, and properties of the interfacial region [157].

Elastomers filled with nanoparticles show a solid-like behavior response, which includes a nonterminal zone of relaxation and a shear-thinning dependence of viscosity on particle concentration and/or dispersion. This behavior arises due to the formation of network structure by polymer–particle or/and particle–particle interactions. The strain dependency of the dynamic viscoelastic properties of elastomers is known as the Payne effect [158] and is well known in elastomers for 40 years. It is well established that rubber-like materials exhibit an appreciable change in their mechanical properties (stress softening) resulting from the first tensile experiment. The well-known phenomenon known as Mullins effect [159] is due to following reasons: (i) physical disentanglement of rubber chains, (ii) decrease in the interactions between polymer molecules and filler surfaces, (iii) filler network breakdown, and (iv) chain scission of rubber molecules.

On examining the viscoelastic behavior of PS/SiO₂, PP/MMT nanocomposites, both percolation threshold and limit of linearity decrease with an increase in the exfoliation state of organoclay platelets whereas they increase with the dispersion of fumed silica by surface grafting of end-tethered chains. From these results on thermoplastic nanocomposites, one could conclude that the filler networking is the primary structural variable controlling their viscoelastic properties. But in the case of elastomers, that is, polymers with long chains and sometimes with particular viscoelastic behavior, the filler network appears to be a second-order structural parameter affecting the viscoelastic response of the nanocomposite. Kalfus and Jancar [160] showed that the modulus recovery time was governed by the chain relaxation processes in the polymer matrix near the filler surface. As a result, in this study, filler agglomeration and/or network is less important representing only a second-order contribution to the nonlinear viscoelastic response of a nanocomposite. It is concluded that the linear and nonlinear rheological properties of polymer nanocomposites are consistent with a network structure of weakly agglomerated particles, which is combined with a mechanism of polymer chain relaxation at the filler surface vicinity governed by the polymer–particle interactions.

1.6 CONCLUSION

Polymer nanocomposites are materials possessing unique properties as new materials and used for academic research as well as for the development of innovative industrial applications. These materials possess characteristic properties of both polymer and filler. Various types of nanomaterials can be used as reinforcing fillers in polymer nanocomposites based on their size, shape dimension, and surface area. In developing these composites, the nanomaterials have a strong tendency to form aggregates due to their large surface area, so in order to improve dispersion stability and compatibility with matrix, their surfaces should be modified either by grafting polymers or by absorption of small molecules, such as surface-modifying agents. Polymer

nanocomposites offer both great potential and great challenges, marking it as a vibrant area of work for years to come. The improvement and application of these composites will depend on how effectively we can handle the challenges. Nanocomposites represent one of the new classes of materials, but further research and development is needed before they gain significant position in the market.

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