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Polymer nanocomposites – synthesis techniques, classification and properties

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Outline:

Introduction

Nanotechnology

Nanotechnology is the engineering at the atomic or molecular level. It is the collective term for a wide range of technologies, processing techniques, and measurements that involve the manipulating of matter at the smallest scale (from 1 to 100 nanometer). The prefix nano has been driven from the Greek word νᾶνος or Latin word nannus, both meaning dwarf. It was adopted as an official SI prefix meaning 10^{-9} of an SI base unit. Nanotechnology is the study of controlling the matter on an atomic and molecular level. Generally, nanotechnology deals with structures and components with size between 1 to 100 nanometer in at least one dimensions, and involves developing, creating or modifying materials or devices within that length scale. Nanotechnology is concerned with the creation of particles and materials at nanoscale dimensions. These particles and materials are referred to as nanoparticles and nanomaterial, respectively, and they exhibit unusual and exotic properties that are not present in traditional bulk materials. Nanotechnology can be defined as systems or processes that provide goods and/or services that are obtained from matter at the nanometer level, *i.e.*, from sizes in the range of one-billionth of a meter [1-2]. According to Drexler, "Nanotechnology is the principle of manipulation of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom-by-atom precision, yielding a variety of nanomachines [1-2]." Nanoscience is the study of the fundamental principles of molecules/atoms and structures with at least one dimension between 1 and 100 nanometers. These structures are termed as nanostructures. Nanotechnology is the application of these nanostructures into useful nanoscale devices [3]. The laws of science are not enough to deal with engineered nanomaterials or nanostructures. Nanomaterials possess a large surface area, a high aspect ratio, and a high surface-to-mass ratio. The unusual features of nanomaterials can significantly influence the physical, chemical, biological, mechanical, and electrical properties [1-2].

Nanotechnology is a wide interdisciplinary field of research, innovation, development and industrial activity that has been growing in a speedy way worldwide for last few years [4-6]. It entails physics, chemistry, biology, material science, colloidal science engineering and electronic processing, composites, application and concepts in which the defining characteristic is one of size or dimension [4]. It involves the fabrication, processing, imaging, measuring and application of materials that are in the size range of up to 100 nm. The term "nanotechnology" was first introduced in 1974 by a Japanese Engineer, Norio Taniguchi. The term implied a new technology which can control materials beyond micrometer scale [4]. In 1959, Richard Feynman gave the ideas of creating nanoscale machines. In his famous lecture in 1959 "There's Plenty of Room at the Bottom", Feynman presented the idea of creating new materials at nanoscale dimensions, which began a variety of nanotechnology discussions, many of which still continue today. In the 1980s, IBM Zurich scientists invented the tunneling microscope, a landmark achievement in nanotechnology development, which allowed scientists and researchers to analyze materials at the atomic or molecular level. Recently, the expenditure on nanotechnology research and development has increased drastically. Research in nanotechnology continues to expand worldwide, and in the next decade, nanotechnology could have a $1 trillion impact on the global economy. Nanotechnology is currently in a very infantile stage. However, we can organize matter on the atomic scale, and there are already numerous products available as a direct result of our rapidly increasing ability to fabricate and characterize feature sizes less than 100 nm [2]. Nanotechnology has the capability to change our standard of life. Some of the latest applications of nanotechnology are energy storage and production, information technology, medical purposes, manufacturing, food and water purification, instrumentation, biomedical and environmental uses. Several nanotechnology-based products already available on the market such as electronic components, nanopaints, storage devices, stain-free fabrics, and medical components [2]. The basic attribute of this technology is the size that makes it so feasible to be used in many different fields. The nano size of the materials provides certain advantages like high surface area and low surface defects in the material, thereby improving the material properties. One of the fundamental aspect of nanotechnology is the creation of new materials having one of the dimension at nanoscale. These materials, known as nanomaterials, are engineered at nanoscale have entirely different properties than their “bulk” counterpart. Nanomaterials are being used in almost everyday objects such as window coatings, sunscreens and other cosmetics, textiles, paint, cutting boards, socks, etc. Nanomaterials may also be found in human hip joints, Organic Light Emitting Diodes (OLEDs) for displays and ear implants, pacemaker and water splitting. The commonly used engineered nanomaterials in consumer products are nanosilver, carbon nanotubes, metal oxides at nanosized (ferrous oxides, titanium dioxide and zinc oxide), silica and gold. Other engineered nanomaterials used in consumer, medical and industrial products are nanocarbon, cerium oxide, nickel, aluminum oxide and the nanoclays copper oxide, iron oxide and quantum dots.

Classification of Nanomaterials

The classification of nanomaterials is based on the number of dimensions, which are in nano range (≤ 100 nm).

- 0D nanomaterials have all the dimension within nanoscale, i.e. no dimension is larger than 100 nm. The most common example of 0D-dimensional nanomaterials is the nanoparticle. These nanoparticles can be crystalline or amorphous, metallic, ceramic, or polymeric.
- 1D nanomaterials have at least one dimension in nano range. This leads to needle like – shaped materials having one dimension at nanoscale. 1D nanomaterials include nanoplatelets, nanorods, nanoclays and nanosheets.
- 2D nanomaterials have two dimensions in nano range. 2D nanomaterials include nanofibers, nanotubes, nanorods and whiskers. Carbon nanotubes are good example of 2D nanomaterials.
- 3D nanomaterials have all three dimension in nano range. 3D nanomaterials include nanogranules, nanoclays and equiaxed nanoparticles.

The nanomaterials can be crystalline or amorphous or polycrystalline. They can composed of a single or multi-phase chemical elements. They could be in various forms and shapes, metallic, ceramic or polymeric.

Nanoparticles

A nanoparticle is a fundamental component in the fabrication of a nanostructure having dimensions between 1 to 100 nm. Nanoparticles are generally the final products of a series of chemical, physical and biological processes [7]. Metallic nanoparticles have different chemical and physical properties than their bulk counterparts (e.g., lower melting temperatures, specific properties, high surface area, mechanical strength etc.). These properties are very attractive for various industrial applications. A nanomaterial (dimension <100 nm) can take many forms such as particle, wire, tubes, rod and sphere. Nanoparticle products generally include metal oxides, quantum dots, silicon dioxide, dendrimers, and some layered structures. In recent years, the development of new nanoparticles has been growing rapidly. The categories of nanoparticles are as below:

Nanomaterials

Materials built with structural components whose size is less than 1 µm in at least one dimension are defined as nanomaterials.

Fullerenes

They are naturally occurring molecules of carbon, in the form of hollow sphere, ellipsoid, or tube. Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. Fullerences are a pure form of carbon molecules in the form of a hollow sphere, tube, ellipsoid, and various other shapes. Spherical Fullerences are termed as buckyballs. Cylindrical Fullerences are called carbon nanotubes. Fullerences are similar to graphite in structure, which is composed of a hexagonal ring that form a three dimensional structure. Fullerences were first synthesized by laser ablation of graphite target in helium gas. However, laser vaporization is also used in fullerence synthesis. The other techniques used in fullerence production are thermal decomposition of hydrocarbon, combustion of hydrocarbon and thermal plasma pyrolysis of hydrocarbon [8].

Carbon Nanotubes (CNTs)

Carbon nanotubes are long, thin cylinders of carbon, and were first discovered by lijima in 1991 in Japan using an arc-discharge method. These are large macromolecules having unique size, shape and possess remarkable physical and mechanical properties. CNTs are a special form of fullerenes, consisting of concentric layers of graphite (multi-walled CNTs) separated by Van der Wall forces. However, CNTs composed of a single layer (Single-walled CNTs, or SWCNTs) were also discovered. CNTs are similar in structure to C_{60} (buckyballs), but they are elongated to form a tubular structure [8]. A single-walled CNT has a diameter of 0.6–5 nm, whereas a multi-walled CNT has an inner diameter of 1.5–15 nm and an outer diameter of 2.5–50 nm. CNTs can be produced in various aspect ratios, and their lengths also vary, depending on the processing technique [8]. Nanotubes have a wide range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). CNTs are a very good example of true nanotechnology, since they are less than 100 nanometer in diameter and can be thinner than 5 nanometer.

Nanowires

Nanowires are extremely thin wires having diameters on the order of few nanometer or less. There are two processes that are generally used to manufacture nanowires: deposition and suspension. Nanowire are composed of either conducting or semiconducting nanoparticles with diameters between 1 to 100 nanometer and high aspect ratios. These wires are also termed as “quantum wires” since quantum effect becomes more dominant at nanoscale. They possess least dimension for efficient transport of electrons and therefore can be used as interconnects in nanoelectronics.

Various types of nanowires are being fabricated including metallic, semiconductor and insulating nanowires.

Quantum Dots

Quantum dots are tiny semiconductor nanostructure that confine the motion of electrons in conduction band, holes in valence band or excitations of bound pairs of conduction band electrons and valence band holes in all three spatial directions. Quantum dots have diameter in the range of 2-10 nanometer (10- 50 atoms) having novel optical, electronic, magnetic and catalyst properties. Quantum dots have discrete quantized energy spectrum and the corresponding wave functions are spatially localized within the quantum dots, but extend over many periods of the crystal lattice. Researchers have found their applications in many areas such as solar cells, transistors and LEDs.

Metallic Nanoparticles

The term metal nanoparticle is used to describe nanosized metals with dimensions (length, width or thickness) within the size range 1-100 nanometers. A nanoparticle is a basic component of a nanostructured material. Generally, the size of a nanoparticle is in the range of 1–100 nm. Metallic nanoparticles exhibit different physical and chemical properties than their bulk counterparts and some of these properties might prove attractive in industrial applications. Nanoparticles possess some unique features, such as high surface area-to-volume ratio, large surface energy, quantum confinement, short-range ordering, etc. The commercially available metallic nanoparticles are silver (Ag), Au, Pt, ZnO, and metal oxides such as copper oxide (CuO), SiO_2, TiO_2, aluminum oxide(alumina) (Al_2O_3), and iron oxides (Fe_3O_4, and Fe_2O_3).

Carbon Black

Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of fossil fuels. It is black in color, finely divided pellet or powder. It is generally used in tires, rubber, many plastic products and printing ink. Generally, anthropogenic combustion of fossil fuel produces a wide variety of particles, including some ultra-fine particles that are compatible with nanoparticle definitions, and therefore referred to as carbon black, having particle size in the range of 10-300 nm [9].

Dendrimers

Dendrimers are a family of nanoscale three dimensional macromolecules with a star-like appearance having highly branched architecture. Dendrimers have three main components: an inner core, an interior structure (branches), and surface group at the exterior surface. By varying these three components, dendrimers of different shapes and sizes can be produced. Their structure greatly impacts their physical and chemical properties. Dendrimers are an ideal candidate for applications in biology, engineering and material science.

Nanoclays

Nanoclays are nanoparticles of layered mineral silicates, have become a class of organic-inorganic hybrid materials. Depending on chemical composition and morphology of particles, nanoclays are organized into several classes such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Nanoclays are a class of hybrid organic-inorganic nanomaterials with potential uses in polymer nanocomposites, as rheological modifiers, gas absorbents and drug delivery carriers. Layered silicate is a generic term referring to synthesized layered silicates (montmorillonite, laponite, and hectorite) as well as natural clays. Montmorillonite is the most common nanoclay used in many materials applications. The plate-like montmorillonite consists of a one-nanometer-thick aluminum silicate layer surface modified with cations having dimensions in length and width that are measured in hundreds of nanometers [10].

Nanocrystals

Nanocrystals are crystalline particles with at least one dimension in nanometers. Nanocrystals have wide range of applications. The properties of nanocrystals can be changed depending on the techniques in their synthesis. They have been used in the manufacture of filters that refine crude oil into diesel fuel. Nanocrystals can also be layered and applied to flexible substrates to produce solar panels. They can be incorporated into electronic devices such as light emitting diodes (LEDs) for energy-efficient lighting, and they are being used in filtration to refine crude oil into diesel fuel. They are also finding application in many other areas such as solar cells, catalysts, and sensors.

Nanocomposites

Nanocomposites are composite materials having one of the phases with dimension in the nanometer range. Nanocomposites are possible alternatives to microcomposites and monolithic due to their outstanding properties. However, the preparation techniques of nanocomposites present challenges due to the control of elemental composition and stoichiometry in the nanophase. Additionally, the discovery of carbon nanotubes in 1991 and their use in the fabricating nanocomposites, added a new interesting feature to this area.

Nanocomposites are materials to which nanosized filler components are added in order to improve the properties of the resulting materials [11]. Nanocomposites are composed of two or more distinct constituents or phases having different physical and chemical properties and are separated by a distinct interface. Their unique properties are not depicted by any of the constituents. The constituent that is generally present in greater quantity is called the matrix. The constituent that is embedded into the matrix material in order to improve the mechanical properties of nanocomposites is called reinforcement (or nanomaterials). Reinforcement is generally in the form of nanosized filler materials. Generally, nanocomposites show anisotropy (properties are directionally dependent) because of the distinct properties of constituents and inhomogeneous distribution of the reinforcement.

The term nanocomposite is extensively used to describe an extremely broad range of materials, where one of the dimension is in nano range. Nanocomposites are generally more advantageous than conventional composites in many aspects. The advantages of nanocomposites are as below [12]:

1. The improvement in properties of the matrix material in nanocomposites can be achieved by the addition of small amount of nanofiller materials compared to conventional composites that require high concentration of micro particle in order to improve properties.

2. Due to the addition of small percentage of nanofiller materials, nanocomposites are much lighter in weight compared to conventional composites.
3. Nanomaterials having size dependent properties enhances thermal, chemical, mechanical, optical, magnetic and electrical properties to a much greater extent than conventional composites.

Nanocomposites are extremely good alternative to conventional composite materials due to their outstanding properties and are finding a wide range of applications in various fields. Nanocomposite systems with carbon nanotubes have been a topic of recent research and development since their discovery in 1991 and there has been a steady and continuous increase in number of publications on this topic, including reviews and patents from time to time. Nanocomposites are also found in nature, for example in the structure of the abalone shell and bone. Nanocomposites differ from conventional composites due to high surface area to volume ratio of the reinforcing nanoparticles and their exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals, metallic nanoparticles, Carbon nanotubes), sheets (e.g. exfoliated clay stacks, graphene) or fibers (e.g. Electrospun nanofibers). The area of the interface between the matrix and nano-reinforcement is typically an order of magnitude higher than the conventional composites. Clays are a group of nanofiller materials which have been extensively used for the preparation of polymer matrix nanocomposites. Polymer/clay nanocomposites have been receiving tremendous attention recently in academia and in industries due to their improved properties compared to conventional composites. Clay minerals are belonging to a main group of silicates with layered structure known as layered silicates. The layered silicates are natural or synthetic mineral materials composed of regular stacks of aluminosilicate layers having high aspect ratio and high surface area. Clay is a soil fraction having particle size of around 2 micrometer and thickness in nanorange generally around 1nm. There are many types of clays with differences in their formula, properties and structures. Polymer/clay nanocomposites can be fabricated in a number of ways including in situ polymerization, melt blending, solution mixing and latex methods.

Types of Nanocomposites

Nanocomposites are classified according to the types of reinforcement materials and matrix materials used in their construction. According to the type of matrix material, nanocomposites are generally classified into following three classes [13]:

1. Polymer Matrix Nanocomposites
2. Ceramic Matrix Nanocomposites
3. Metal Matrix Nanocomposites

Polymer Matrix Nanocomposites:

Polymer nanocomposites are materials that have polymer as a matrix material and nanoadditives are used as reinforcement material. The additives can be one-dimensional (nanotubes and fibers), two-dimensional (layered materials like clay) or three-dimensional (spherical particles). Polymer nanocomposites have been gaining considerably attention both in academia and in industries, due to their outstanding mechanical properties such as high elastic stiffness and strength with a small concentration of nanoadditives. The other excellent properties of polymer nanocomposites are barrier resistance, flame retardancy, wear resistance, magnetic, electrical and optical properties.

A typical polymer composite is a combination of polymer (matrix) and a filler (reinforcement). Polyamide is a thermoplastic polymer, and carbon and glass fiber are generally used as reinforcement materials. In aerospace industry, carbon fibers are extensively used as reinforcement materials. The choice of reinforcement material depends on the applications. The polymer matrix and fillers are generally bonded by weak intermolecular forces, however, in some cases chemical bonding is employed, as well. If the filler material in composite is dispersed on an atomic or molecular level (nanometer level) and chemical bonding with the matrix material is created, then remarkably improvements in the mechanical properties of the composite material and some new and unexpected or exotic properties can be achieved. To achieve high strength, clay minerals (montmorillonite, saponite, hectorite etc) are being used as filler materials. A layer of silicate clay mineral is around 1nm thickness and composed of platelets of approximately 100 nm in width, therefore, it displays a high aspect ratio [14]. In comparison, a glass fiber is approximately 4×10^9 times the size of a typical silicate layer having 13 micrometer diameter and 0.3 millimeter length.

Polymers have outstanding properties such as lightweight, high durability, easy processing, corrosion resistance, ductility and low cost. Compared to ceramics and metals, polymers have relatively poor mechanical, thermal and electrical properties. Polymers also have poor gas barrier properties, heat resistance and fire performance properties. Polymers are less dense than ceramics and metals, they have a low coordination number and lightweight atoms of carbon and hydrogen as a backbone, which makes them find applications as structural components and construction materials in lightweight applications such as automobile, defense, aerospace and electronics [15]. Sometimes, unprecedented combinations of properties have been observed in some polymer matrix nanocomposites such as addition of a very small amount of mica-type silicates (0.03- 0.04 %) in epoxy increases modulus in rubbery region by approximately 450%. Nanocomposites development led to the significant progress in the chemical processing of nanoparticles. Recent interest in polymer nanocomposite has begun initially with fascinating observations involving exfoliated clay and carbon nanotubes, exfoliated graphite and nanocrystalline metals. In polymer nanocomposites, the synergistic advantage of “nano-effect” relative to large scale modification is an important factor affecting the properties of nanocomposites [16]. Experimental investigations have shown that nanoscale additives bring new phenomena, which changes of the material properties. The inclusion of nanoparticles with high surface area, high surface energy and often with anisotropic geometry in the polymer matrix decreases the interparticle distance and increases polymer matrix interaction strength. Therefore, polymer nanocomposites with completely new set of properties suitable for new applications and also expand the performance space of traditionally filled polymers [17]. The micromechanics theories depend on the idea that the properties of composites are functions of properties of constituents such as volume fraction of components, shape and arrangement of inclusions and matrix-fiber interface. These theories predict that the properties of composites are independent of the size of inclusions. This could be true with micro size reinforcements, but may not be true with nano size reinforcement. Fabricating good polymer matrix nanocomposites is a challenging issue. Researchers have tried many techniques to fabricate polymer matrix nanocomposites such as melt mixing, in situ polymerization, mixing filler materials during electrospinning, and many other approaches. Vollenberg and Heikens produced nanocomposites samples by thoroughly mixing filler particles with polymer matrix. They used polystyrene (PS), styrene–acrylonitrilecopolymer (SAN), polycarbonate (PC) and polypropylene (PP) with alumina beads having 35nm and 400nm dimension as filler materials [18]. The average volume fraction of filler particles was maintained at 25%. Sample preparation consisted of dissolving polymers in a polar solvent and mixing in the beads for several hours on a magnetic stir. The mixture was then poured over a large surface container to allow the solvent to evaporate and then it was subsequently dried under a vacuum at 100◦C. Pure polymer was then added to samples to achieve the desired particle volume fractions. In literature, many processes have been described for the preparation of polymer nanocomposites including layered materials and those that contain carbon nanotubes. The common ones are 1) In situ polymerization; 2) Intercalation of polymer from solution; 3) Direct mixing of polymer and fillers; 4) Melt intercalation; 5) Template synthesis; and 6) Sol-gel process. The melt blending is a relatively new process of nanocomposite fabrications. This process involves the melting of polymer to form a viscous liquid. The nanoparticles are dispersed into polymer matrix by means of high shear rate along with diffusion at high temperature. The nanocomposites are then fabricated by either compression molding or injection molding.

Properties of Polymer Matrix Nanocomposites

The properties of nanocomposites do not depend on the properties of individual components but also depends on the following parameters [18-19]:

- Process used in nanocomposite fabrication
- Types of filler materials and their orientations
- Degree of mixing of two phases
- Type of adhesion at the matrix interface
- Volume fraction of nanoparticles
- Nanoparticle characteristics
- Nature of the interphase developed at the matrix interface
- Size and shape of nanofiller materials and
- Morphology of the system

In order to achieve enhanced properties of nanocomposites, the nanosized particles should be dispersed and distributed in the matrix material properly, otherwise there will be agglomeration of particles and the properties of nanocomposites will deteriorate. These aggregates will act as defects and limits the property enhancement of nanocomposite, therefore to achieve maximum property enhancement, the nanoparticles should be homogeneously dispersed in the matrix. Figure 4.1 shows different types of nanoparticles in the matrix material, (a) good distribution but poor dispersion (b) poor distribution and poor dispersion, (c) poor distribution but good dispersion, and (d) good distribution and good dispersion [20].

The other important factor that affect the nanocomposite property enhancement is the nature of interface between matrix and filler material. The most common feature of polymer matrix nanocomposites is the existence of phase border between matrix and filler material and the development of interface layer between the two. The properties, composition and microstructure at the interface vary across the interface region and are different from both matrix and filler. If the interface region has good bond between matrix and filler material the overall properties of the nanocomposite will be much profound. Most of the interphase properties depend on the bound surface and therefore the nanocomposite properties can be tailored by optimizing the interfacial bond between the nanofiller and polymer matrix. The interaction between the interconnecting phases depends on the ratio of surface energy of filler and matrix. Nanosized particles have high surface area and the total surface area of a nanoparticle determines the extent of interface phenomenon contributing to the properties of nanocomposites [21-22].

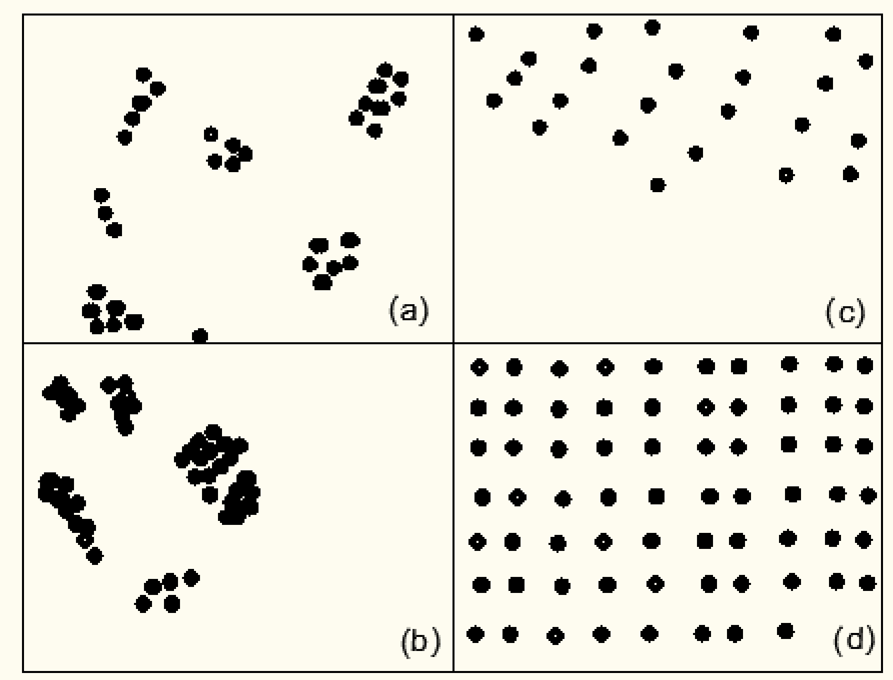

FIGURE 4.1
Distribution and dispersion of nanoparticles in the matrix

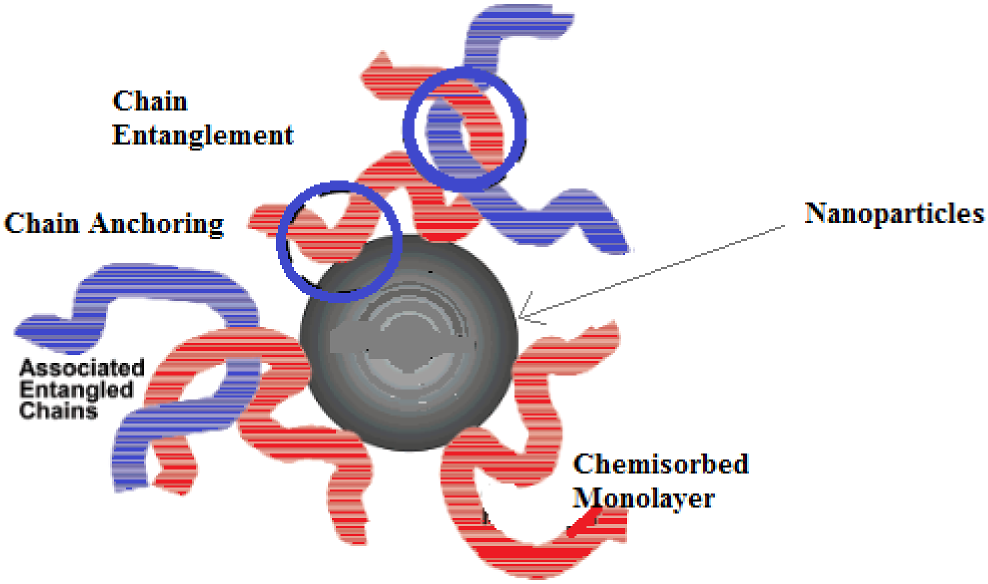

FIGURE 4.2
Interphase region between filler and polymer matrix

As can be seen in Figure 4.2, the structure of the region between filler and polymer matrix consists of flexible polymer chains, typically in sequences of adsorbed segments and unadsorbed segments. Adsorbed segments have point contact with nanoparticle surface in the form of anchors/ trains and unabsorbed segments have no surface contact and exist as loops and tails entangles with other polymer chains in their vicinity. The thickness of the interphase region depends on many factors such as flexibility, energy of adsorption, and the extent of polymer chain entanglement. The interface structure determines the stress or load transfer from matrix to filler [22]. The host polymer needs to have very good interaction with the nanofiller material surface either chemically or physically in order to have good polymer properties. Good adhesion at the interface improves interlaminar shear strength, corrosion resistance, fatigue, dielectric properties, thermal stability, and flame retardancy at low filler-volume fraction [21, 23, 24, 25].

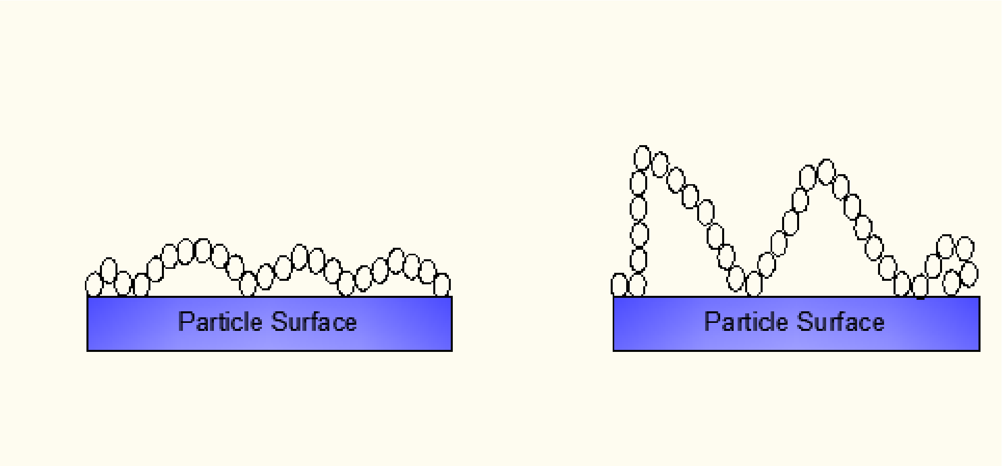

FIGURE 4.3
Different types of polymer matrix adhesion with the nanoparticle surface

Figure 4.3 shows two different types of polymer matrix adhesion with the surface of nanofiller material, (a) strong adhesion of polymer chains with nanoparticle surface, and (b) weak adhesion of polymer matrix with the surface of nanofiller material.

Strong interaction of polymer chain with nanoparticles surface makes flat dense layer residing on the nanoparticle surface. However, poor interaction results in a lower density region with polymer loops and tails extending into the matrix. It has been reported in the literature that drastic changes in the particle properties can be observed when the particle size is in the nanorange. Moreover, as the dimension reaches the nanorange, the interaction at the phase boundary improved to a great extent resulting in the enhancement of materials property. The extent to which the host polymer properties alter also depends on the aspect ratio, shape and orientation of nanoparticles. High aspect ratio nanoparticles have high surface area compared to low aspect ratio nanoparticles and high aspect ratio plays an important role in enhancing the properties of nanocomposites. Asymmetric nanoparticles such as layered silicates or carbon nanotubes enhance polymer properties (viscosity, shear modulus, tensile strength) to a great extent than symmetrical nanoparticles with spherical shape etc. Compared with elongated rod like nanoparticles and highly symmetric nanoparticles, sheet like nanoparticles enhances polymer properties such as gas permeability and mechanical properties to a great extent [26, 27].

The properties of nanocomposites depend on their microstructure. The morphological characteristic nature of the composite system describes the structure property relationship of polymer nanoplatelets type of nanocomposites. A good dispersion of nanomaterial is hard to achieve, especially in non-polar polymer, however, uniform dispersion of nanoplatelets ensure good quality of composites. In the case of nanocomposites containing layered reinforcements, depending on processing techniques, nature of the components (layered silicate, organic cation and polymer matrix), dispersion techniques,and the interaction between polymer matrix and layered nanomaterial, the microstructure of nanocomposites can be classified as exfoliated, intercalated and phase separated (aggregated) [28]. When the polymer cannot be intercalated between the silicate layers, a phase separated (aggregated) composite is formed, whose properties are almost the same as that of conventional microcomposites (Figure 4.4(a)) [28]. In intercalated nanocomposites, the polymer chains intercalate into the silicate layers in a crystallographically regular order, regardless of the clay to polymer ratio (Figure 4.4(b)) [28]. A well-ordered multilayer microstructure is formed with alternating polymeric and clay layers. In an exfoliated nanocomposites, the clay layers are completely and uniformly dispersed in the polymer matrix. The clay layers are separated in polymer matrix by an average distance that generally depends on clay loading. Generally, the clay layers content in an exfoliated nanocomposite is lower than that of an intercalated nanocomposites. Figure 4.4 shows different types of dispersion of clay layers in polymer matrix.

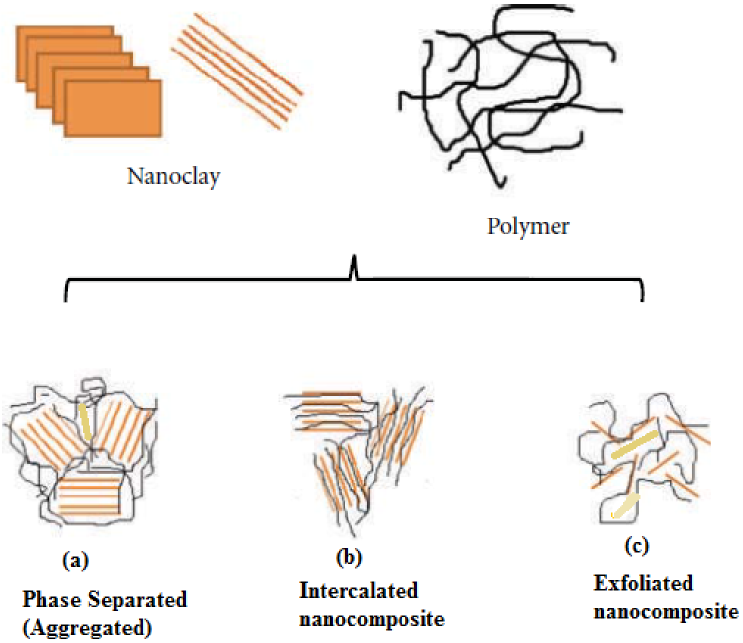

FIGURE 4.4
Different types of dispersion of clay layers in polymer matrix

Types of Polymer Matrix Nanocomposites

The major component in polymer matrix nanocomposite is polymer itself. There are many varieties of polymers used in the preparation of polymer matrix nanocomposites. These polymers are listed below [29]:

1. Thermoplastics
2. Thermosets
3. Elastomers
4. Natural and Biodegradable polymers

The choice of polymer matrix material for preparing polymer matrix nanocomposites for a specific application is generally guided by their mechanical, electrical, magnetic, optical, biocompatibility, chemical stability and functionalization. Thermoset based nanocomposites are generally most common nanocomposites and are used in many applications, but recently thermoplastic-based nanocomposites have attracted much of the research interest both in industry and academia. The properties of polymers mainly depend on the polymer structure, which in turn depends on the chemical composition, surface morphology and processing parameters. The difference between thermoplastic and thermosets polymer is that they respond entirely in a different way to heat and this is mainly due to the difference in their molecular structure [30-31].

- *Thermoplastics:*

Thermoplastics soften when heated and become more fluid as heating continued. The curing process of thermoplastics is completely reversible as no cross linking takes place. Thermoplastics soften on heating and solidify and harden on cooling. This property allows thermoplastics to be remolded and recycled without affecting the properties.

- *Thermosets:*

Thermosets contain polymer that cross-link together during curing process and form an irreversible chemical bond. These polymers do not soft or melt on heating but breakdown chemically at high temperature. Thermosets have improved mechanical properties, high chemical and heat resistance properties. Thermoset are generally rigid and brittle compared to thermoplastics.

Ceramic Matrix Nanocomposites

Ceramic matrix nanocomposites with at least one phase having nano dimension are a new generation of engineering materials, having a wide range of applications in industrial sector. The microstructure of nanoceramic composites results in outstanding electrical and mechanical properties. Many methods have been reported in literature for the preparation of ceramic matrix nanocomposites. Generally, the common methods used in microcomposites fabrications are conventional powder method, polymer precursor route, spray pyrolysis, and chemical methods such as sol-gel process, colloidal and precipitation approaches and template synthesis [28]. Some common ceramic matrix nanocomposites include AL_2O_3/SiO_2, SiO_2/Ni, Al_2O_3/TiO_2 and Al_2O_3/SiC [29]. After the discovery of carbon nanotubes (CNT), they have been widely used in nanocomposite fabrications. Some common examples of CNT based ceramic matrix nanocomposite include Al_2O_3/CNT, $MgAl_2O_4$/ CNT and MgO/CNT.

Metal Matrix Nanocomposites

Metal matrix nanocomposites are materials reinforced by nanoparticles consisting of ductile metal or alloy matrix in which nanoparticles reinforcement is implanted. These composites consist of metal/alloy matrix filled with nanoparticles, display physical, chemical and mechanical properties entirely different from those of matrix material. The nanoparticles are generally used to improve wear resistance, mechanical properties and damping characteristics. Metal matrix nanocomposites are being investigated by researchers recently, owing to their superior properties due to nanoparticle embedment, are finding wide range of applications in structural components [28]. At nano-level the interaction of particles with dislocations becomes important and results in remarkable improvement in mechanical properties. The nanoparticles act as a barrier in dislocation movement and thereby improve the mechanical properties. The common techniques used for the processing of metal matrix nanocomposites are spray pyrolysis, liquid metal infiltration, vapor techniques, rapid solidification, electrode position and chemical methods, which include colloidal and sol-gel methods [28]. Some common metal matrix nanocomposites include Fe-Cr/Al_2O_3, Ni/Al_2O_3, Fe/MgO, Al/CNT and Mg/CNT.

Polymer Matrix Nanocomposite Processing Techniques

Polymer matrix nanocomposites can be fabricated either by chemical or mechanical process. Uniform and homogeneous dispersion of nanoparticles in the polymer matrix is one of the major problem encountered in polymer nanocomposite fabrication. The Nanofillers have a tendency to aggregate and form micron size filler cluster, which limit the dispersion of nanoparticles in the polymer matrix thereby deteriorating the properties of nanocomposites. Researchers have made many attempts to disperse nanofillers uniformly and homogeneously in the polymer matrix by chemical reactions, complicated polymerization reactions or surface modification of filler materials [32]. Mostly polymer nanocomposites are fabricated by the following four methods.

1. Intercalation method
2. In situ Polymerization
3. Sol Gel method
4. Direct Mixing of polymer and Nanofillers

Intercalation Method

Intercalation method generally involves the dispersion of nanoplatelets types of nanomaterials into the polymer matrix. It is well-known that incorporation of clays (nanomaterial) into polymer matrices improves the bulk properties such as stiffness, shrinkage and flammability. Intercalation is a top down approach and requires surface modification of nanoplatelets for homogeneous dispersion of plate-like nanofillers in the polymer matrix. Intercalated morphology occurs when polymer chains diffuse into the gallery spacing of layered structure. The nanoplatelets can be homogeneously dispersed by the following two techniques [33-35].

- *Chemical Technique:* This technique involves the in-situ polymerization method in which nanoparticles are dispersed in monomer and then polymerization reaction takes place. In this method, nanoplatelets are dispersed into polymer followed by additional polymerization process. The nanoplatelets are swollen in monomer solution and the polymer formation occurs between the intercalated sheets by polymerization method.

- *Mechanical Technique:* In this method, direct intercalation of polymer with nanoplatelets takes place through solution mixing. The polymer is dissolved in a co-solvent and nanoplatelets sheets are swollen in the solvent and these two solutions are mixed together, the polymer chains in the solution intercalate into the nanoplatelets layers and displace the solvent.

Melt Intercalation Method

Melt intercalation is a promising method extensively used in the industry. This method involves mixing the nanofillers (clays) into the polymer matrix at molten temperature. In this method, mixture of polymer and nanofibers are annealed either statically or under shear. This method is compatible with current industrial processes, such as extrusion and injection molding and it allows the use of polymers, which are not suitable for in situ polymerization or solution intercalation. Melt blending is a similar process. It involves the melting of polymer powder or pellets to form a viscus solution and nanofillers are added into polymer solution by high shear rate combined with high temperature diffusion. The final shape of components can be fabricated by compression molding, injection molding or fiber production technique.

In Situ Polymerization Method

In situ polymerization involves the swelling of the nanofillers in monomer solution since the low-molecular weight monomer solution can easily seeps in between layers causing swelling [35]. The resulting mixture is polymerized either using radiation, heat, initiator diffusion or by organic initiator. The monomer is then polymerized between interlayers thereby forming either exfoliated or intercalated nanocomposites. In Situ template synthesis is a similar method. In this method, the clay layers are synthesized in the presence of polymer chains. Both polymer matrix and clay layers are dissolved in an aqueous solution and gel is generally refluxed at high temperature. The polymer chains are trapped inside the clay layers and nucleation and growth of clay layers take place on the polymer chains at high temperature. The only drawback of this process is that high temperature synthesis causes decomposition of polymer.

Sol- gel Method

Sol- gel method is a bottom up approach and it is based on an opposite principle than all the previous methods. The term sol-gel is associated to two relations steps, sol and gel. Sol is a colloidal suspension of solid nanoparticles in monomer solution and gel is the 3D interconnecting network formed between phases [35]. In this method, solid nanoparticles are dispersed in the monomer solution, forming a colloidal suspension of solid nanopartices (sol), they form interconnecting network between phases (gel) by polymerization reactions followed by the hydrolysis procedure. The polymer nanoparticle 3D network extends throughout the liquid [35]. The polymer serves as a nucleating agent and promotes the growth of layered crystals. As the crystals grow, the polymer is seeped between layers and thus nanocomposite is formed.

Direct Mixing of Polymer and Nanofillers

Direct mixing of a polymer matrix and nanofillers is a top down approach of nanocomposite fabrication and it is based on the breakdown the aggregated nanofillers during mixing process [32, 35]. This method is suitable for fabricating polymer matrix nanocomposites and it involves two general ways of mixing the polymer and nanofillers. One way is mixing a polymer, in the absence of any solvents, with nanofillers above the glass transition temperature of the polymer, generally called melt compounding method [32, 35]. The other way involves mixing of polymer and nanofillers in solution employing solvents, generally called solvent method/solution mixing [35].

Melt Compounding

This method involves nanofibers addition to the polymer above the glass transition temperature. In this kind of method, the shear stress (hydrodynamics force) is induced in the polymer melt by viscus drag, and this shear stress is used to breakdown the nanofiller aggregates and thereby promotes homogeneous and uniform nanofiller dispersion in the polymer matrix.

Solvent Method

In this method, nanoparticles are dispersed in the solvent and polymer is dissolved in a co-solvent. The resulting nanocomposites are recovered from solvent through solvent evaporation or by the solvent coagulation method. In this method, the shear stresses induced in the polymer matrix are lowered compared to that in melt compounding. The nanofillers are pre-dispersed in the solvent by sonication in order to breakdown the nanofiller aggregates [35].

The polymer nanocomposites fabricated by one of the above methods are finally processed by conventional manufacturing methods like injection molding, calendaring, casting, compression molding, blow molding, rotational molding, extrusion molding, thermoforming, etc [35].

Conclusions

Nanotechnology is the study and control of matter at dimensions of 1 to 100 nanometer. When materials are reduced to nanosized they display some unusual and exotic properties due to “nano-effect”. The field of nanotechnology has become one of the most famous area of research and innovation, recently. Polymer science is an integral part of nanotechnology. Polymer composites are made by the combination of a polymer and synthetic or natural inorganic filler materials. Filler materials are employed in order to improve the properties of polymer composites. In recent years, polymer nanocomposites have attracted great interest, both in industry and in academia, since they exhibit remarkable improvement in properties, when compared to conventional microcomposites. Polymer nanocomposites contain nanofiller materials, which cause “nano-effect” and drastically improve nanocomposite properties. In this chapter, the classification of nanomaterials has been discussed and all types of nanomaterials have been elaborated. New technologies require materials that have novel properties and nanomaterials possess novel properties, which help in improving the properties and performance of components compared to conventionally processes components. In this context, nanomaterials are the most suitable materials to meet the emerging demands arising from scientific community. In this chapter, the classification of nanocomposites based on matrix materials has been discussed along with their processing techniques. However, some of these techniques pose challenges as far as the dispersion of nanophase in polymer matrix is concerned. Thus giving opportunities for researchers to overcome this problem being encountered with nanosized materials. Nanocomposites offer improved performance compared to conventional composites and monolithic counterpart. Polymer nanocomposite have already being used in many industrial sectors and their applications have been rising drastically.

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