

Chunyu Li

Department of Mechanical
Engineering and Center for
Composite Materials
University of Delaware
Newark, Delaware

Jianjun Li

Center for Composites and
Structures
Harbin Institute of Technology
Harbin, China

Yanju Liu

Center for Composites and
Structures
Harbin Institute of Technology
Harbin, China

Pallavi Mavinakuli

Department of Chemical
Engineering
Lamar University
Beaumont, Texas

Hua-xin Peng

Advanced Composites Centre for
Innovation and Science
Department of Aerospace
Engineering
University of Bristol
Bristol, United Kingdom

Basavarajaiah Siddaramaiah

Department of Polymer Science and
Technology
Sri Jayachamarajendra College of
Engineering
Mysore, India

Yong Tang

Composite Materials and
Structures Laboratory
Department of Mechanical,
Materials and Aerospace
Engineering
University of Central Florida
Orlando, Florida

Erik T. Thostenson

Department of Mechanical
Engineering and Center for
Composite Materials
University of Delaware
Newark, Delaware

Suying Wei

Department of Chemistry and
Physics
Lamar University
Beaumont, Texas

Yansheng Yin

Institute of Marine Materials
Science and Engineering
Shanghai Maritime University
Shanghai, China

D. Zhang

Integrated Composites Laboratory
Lamar University
Beaumont, Texas

Jiahua Zhu

Integrated Composites Laboratory
Lamar University
Beaumont, Texas

1**Introduction****Jinsong Leng and Jianjun Li**

Harbin Institute of Technology

Alan kin-tak Lau

*University of Southern Queensland
Hong Kong Polytechnic University*

CONTENTS

1.1 Overview.....	1
1.2 Classification of Nanomaterials and Nanostructure.....	2
1.3 Nanomaterials from Academia to Industry.....	4
1.4 Nanocomposites.....	6
1.5 Multifunctional Polymer Nanocomposites.....	7
1.6 Fabrication of Polymer Nanocomposite.....	14
1.7 Future Trends.....	17
References.....	17

1.1 Overview

The nano era, similar to the mid-industrial steel era, not only stands for great technical innovations but also indicates the future trend of existing technologies. It is believed that this period will dominate and transform people's daily lives. "Nano" is a unit of length defined as 10^{-9} m. To give you an idea of how small it is, the width of a human hair is 10^6 nm, and the size of an atom is 0.1 nm.

In recent decades, the development of microscopes has enabled scientists to observe the structures of the materials at nanoscale and investigate their novel properties. In the early 1980s, IBM (Zurich) invented the scanning tunneling microscope, which was the first instrument that could "see" atoms. In order to expand the types of materials that could be studied, scientists invented the atomic force microscope. Now, these instruments can be used to observe the structures and different properties of materials at nanometer scale. Physics reveals big differences at the nanometer scale, and the properties observed on a microscopic scale are novel and important. For example,

quantum mechanical and thermodynamic properties have pushed forward the development of science and technology in the 20th century.

Nanotechnology means the study and application of materials with structures between 1 and 100 nm in size. Unlike bulk materials, one can work with individual atoms and molecules and learn about an individual molecule's properties. Also, we can arrange atoms and molecules together in well-defined ways to produce new materials with amazing characteristics. For example, nanotechnology has produced huge increases in computer speed and storage capacity. That is why "nano" has attracted attention in the research fields of physics, chemistry, biology, and even engineering. This word has entered the popular culture and can be found in television, movie, and commercial advertisements. Politicians and leaders around the world have realized the importance and urgency of developing nanoscience and nanotechnology, so countries have promoted research in nanoscience and nanotechnology in their universities and laboratories. With the huge increase in funding, scientists are pursuing nano research intensively, and the rate of discovery is increasing dramatically.

1.2 Classification of Nanomaterials and Nanostructure

The main classification of nanomaterials can be described as the following: carbon-based materials, nanocomposites, metals and alloys, nanopolymers, and nanoceramics. Carbon-based materials refer to carbon black, fullerenes, single-walled or multiwalled carbon nanotubes, and other carbides. Carbon nanotubes (shown in Figure 1.1), discovered in 1991 by S. Iijima, are hollow cylinders made of sheets of graphite [1]. The dimensions are variable, and one nanotube can also exist within another nanotube, which leads to the formation of multiwalled carbon nanotubes. Carbon nanotubes have amazing mechanical properties due to strength of the sp^2 carbon-carbon bonds. Young's modulus and the rate of change of stress with applied strain represent the stiffness of a material. The Young's modulus of the best nanotubes can reach 1000 GPa, which is approximately five times higher than the Gpa of steel. The tensile strength can be as high as 63 Gpa, and this value is around 50 times higher than steel. Depending on the graphite arrangement around the tube, carbon nanotubes exhibit varying electrical properties and can be insulating, semiconducting, or conducting. Also, carbon nanotubes are interesting media for electrical energy storage due to their large surface area, and they are still being investigated as a hydrogen storage medium.

Organic-inorganic nanocomposite is the fast-growing area of current materials research. Significant effort is directed at developing synthetic approaches and controlling their nanoscale structures. The properties of nanocomposite materials are determined not only by the properties of their individual

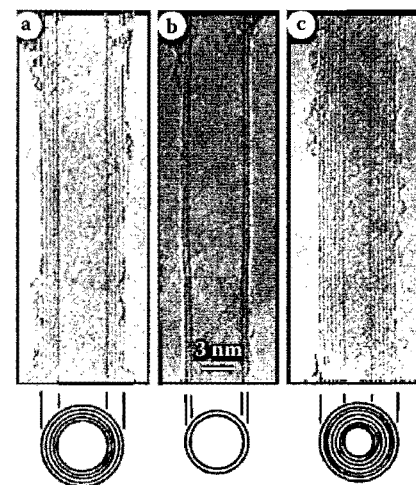


FIGURE 1.1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross section of each tubule is illustrated. (a) Tube consisting of five graphitic sheets, diameter 6.7 nm. (b) Two-sheet tube, diameter 5.5 nm. (c) Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm). (Reprinted with permission from Iijima, S., *Nature*, 1991, 354, 56-58. Copyright 1991 Nature Publishing Group.)

components but also depend on their morphology and interfacial characteristics. The rapid research in nanocomposites has already generated many exciting new materials showing novel properties. It is also possible to discover new properties that are still unknown in the parent constituent materials.

Metal and alloy nanomaterials generally include gold, silver, magnetic iron-based alloys, and magnesium-based alloys. Gold and silver nanoparticles can be easily prepared, and they are promising probes for biomedical applications. Unlike other fluorescent probes such as organic dyes, gold and silver nanoparticles do not burn out after long exposure to light. Gold nanoparticles have already been used as ultrasensitive fluorescent probes to detect cancer biomarkers in human blood. Iron, cobalt, and their alloys are classes of magnetic nanoparticles whose magnetic performance can be modified by controlling synthesis method and chemical structure of the materials. In most cases, the magnetic particles ranging from 1 to 100 nm in size may display superparamagnetism.

Polymers are large molecules (macromolecules) composed of repeating structural units typically connected by covalent chemical bonds. They are widely used in our lives and play an important role in industry. The Nobel Prize in Chemistry in 2000 was awarded for the discovery and development of conductive polymers. In future, one can use such new exciting materials based on conductive polymer technology. In nanostructured polymers, the

attractive force between polymer chains plays an important role in determining their properties. When inorganic or organic nanomaterials are dispersed in the polymers, the nanostructures of polymers can be modified and the desired properties can be obtained.

Nanoceramics considered in the study are oxide and non-oxide ceramic materials. Since nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, they can exhibit novel properties. One important class of nanoceramics is semiconducting materials such as ZnO, ZnS, and CdS; they are synthesized by different methods, and the scientist can control their size and shape easily. They show quantum confinement behavior in the 1–20 nm size range. For such materials, the focus is on the production and application of ultrathin layers, fabrication, and molecular architecture.

Nanostructure is defined as an object of intermediate size between molecular and microscopic (micrometer-sized) structures. Based on the different shapes, generally they can be classified into nanoparticle, nanofiber, nanoflake, nanorod, nanofilm, and nanocluster types, and the typical photos are shown in Figure 1.2 [2–4]. Materials with different nanostructures can have obviously different properties, so one of the tasks scientists face is to find the relationship between properties and structure. We know that the structure of materials will determine their properties, and the properties of materials can reveal their structure. Thus, it is necessary to focus on exploring size-controllable and shape-controllable nanomaterials.

1.3 Nanomaterials from Academia to Industry

The general meaning of synthesis and assembly of nanomaterials is engineering materials with novel properties through the preparation of material at the nanoscale level. In fact, nanomaterials already existed before the advanced microscope was invented. The problem is that scientists cannot observe their nanometer structures directly at the moment. Research in nanomaterials and their novel properties is motivated by understanding how to control the building blocks and enhance the properties at the macroscale. For example, scientists can increase the magnetic storage ability, catalytic enhancement, electronic or optical performance, hardness, and ductility by controlling the size and method of assembly of the building blocks.

The most frequent techniques used in the laboratory to synthesize nanomaterials include chemical vapor deposition, physical vapor deposition, sol-gel technique, and precipitation from the vapor and supersaturated liquids. These techniques have been applied in the industry for the preparation of nano products ranging from electronics to drug delivery systems. There are several reviews on the synthesis and assembly of nanomaterials [5–8].

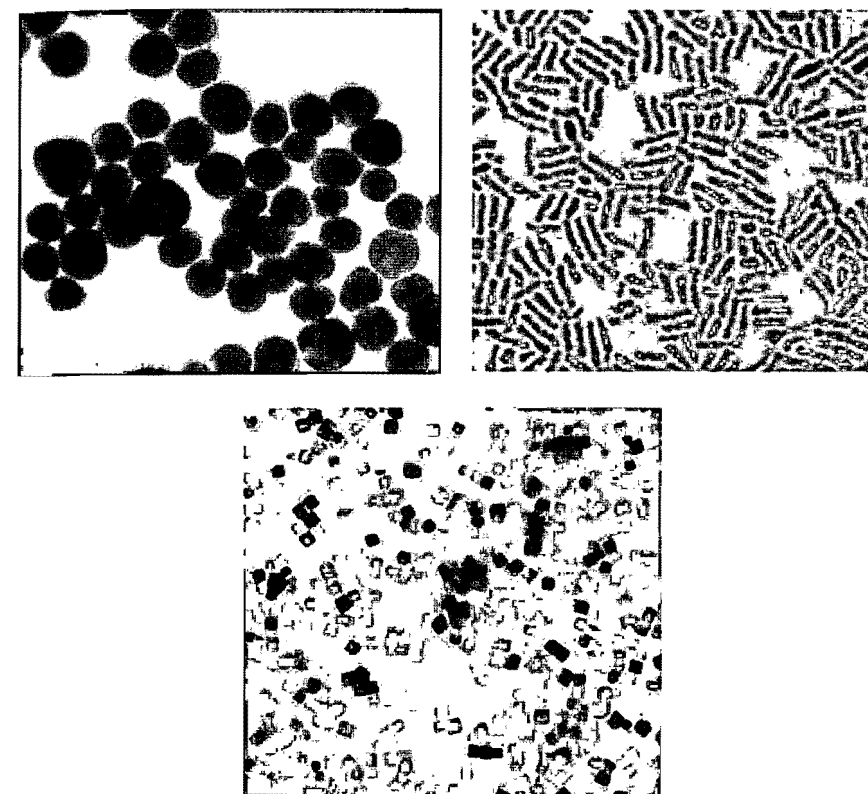


FIGURE 1.2

(Top left) TEM image of 20 nm Au nanoparticles produced by the Turkevich method. (Reprinted with permission from Hodak et al., *J. Phys. Chem. B*, 2000, 104, 9954. Copyright 2000 American Chemical Society); (Top right) CdSe quantum rods grown from the dots by a secondary injection and subsequent growth for 23 h. (Reprinted with permission from Peng, Z. A. and Peng, X., *J. Am. Chem. Soc.*, 2001, 123, 1389. Copyright 2001 American Chemical Society); (Bottom) TEM image of nanocrystalline KMnF_3 . (Reprinted with permission from Carpenter, E. E., Ph.D. thesis, University of New Orleans, New Orleans, LA, 1999. Copyright 1999 Everett E. Carpenter.)

In the global market for nanomaterials, conventional materials such as SiO_2 , TiO_2 , Fe_2O_3 , and ZnO are the main products that make the greatest initial commercial impact. The reason is that these nanoceramics can be easily synthesized, and the cost of production is lower. In future, the possibility of incorporating “smart” features in nanomaterials should be explored. Smart materials can also be termed *intelligent* materials. Such materials have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, light, magnetic fields, or electric fields. Smart materials, including piezoelectrics, electrostrictors, magnetostrictors, and shape memory alloys, can perform sensing and actuating functions. It is believed that the smart materials with nanostructures will dominate our lives.

1.4 Nanocomposites

Composite materials (or composites for short) are combined from two or more constituent materials that have significantly different physical or chemical properties. The constituent materials will remain separate and distinct at a macroscopic level within the finished structure. Generally, two categories of constituent materials, matrix and reinforcement, exist in the composite. The matrix materials maintain the relative positions of the reinforcement materials by surrounding and supporting them, and conversely the reinforcements impart their special mechanical or physical properties to enhance the matrix properties. Thus, the composite will have the properties of both matrix and reinforcement, but the properties of a composite are distinct from those of the constituent materials. Thousands of years ago, people used straw to reinforce mud in brick making to increase the strength of the brick.

A nanocomposite is defined such that the size of the matrix or reinforcement falls within the nanoscale. The physical properties and performance of the nanocomposite will greatly differ from those of the component materials. According to the type of matrix, nanocomposites can be classified into ceramic matrix nanocomposites, metal matrix nanocomposites, and polymer matrix nanocomposites.

In ceramic matrix nanocomposites, the main volume is occupied by ceramics including oxides, nitrides, borides, and silicides. In most cases, a metal as the second component is combined into ceramic matrix nanocomposites. Ideally, the metal and the ceramic matrix are finely dispersed in each other to form a nanocomposite that has improved nanoscopic properties, including optical, electrical, and magnetic properties.

In metal matrix nanocomposites, ceramics are often used as reinforcement and matrices are based on most engineering metals, including aluminum, magnesium, zinc, copper, titanium, nickel, cobalt, and iron. Depending on the properties of the matrix metal or alloy and of the reinforcing phase, the metal matrix nanocomposites can have the features of low density, increased specific strength and stiffness, increased high-temperature performance limits, and improved wear-abrasion resistance. Compared with polymer matrix composites, metal matrix composites can offer higher modulus of elasticity, ductility, and resistance to elevated temperature. However, they are more difficult to process and are more expensive.

Polymer composites are generally made of fiber and matrix. Usually glass, but sometimes Kevlar, carbon fiber, or polyethylene, is used as the fiber. The matrix usually refers to a thermoset such as an epoxy resin, polydicyclopentadiene, or a polyimide. The fiber is embedded in the matrix so as to increase the strength of matrix. Such fiber-reinforced composites are strong and light, and they are even stronger than steel, but weigh much less. This means that composites can be widely used in industry for their high strength-to-weight

ratio. For example, reinforced polymer composite is used in the automotive industry to make automobiles lighter.

1.5 Multifunctional Polymer Nanocomposites

The purpose of producing polymer nanocomposites is to give the composite multifunctional properties, so nano inorganic or organic powders or films with special physical properties are combined with polymers to form polymer nanocomposites. Long ago, people living in South and Central America fabricated polymer composites. They used natural rubber latex, polyisoprene, to make gloves, boots, and raincoats, but one will feel uncomfortable if he wears a raincoat just made from the single polymer. Then, a young man Charles Macintosh used two layers of cotton fabric and embedded them in natural rubber to fabricate a composite with three-layered sandwich structure. Thus, the raincoats made from composites have the advantages of the two components: waterproofing of rubber and comfort of the cotton layers. From this story, we know that the polymer composites with designed structures have the properties of a polymer matrix and inorganic or organic reinforcement. In multifunctional polymer composites, the reinforcements impart their special mechanical, optical, electrical, and magnetic properties to the composite. The polymer matrix holds the reinforcements and retains the properties of polymer; for example, polymer matrix can absorb energy by deforming under stress, thus overcoming the disadvantages of the brittleness of the reinforcement.

The current research emphasis and theoretical work on polymer nanocomposites is to find relationships between the effective properties of polymer composites (such as Young's modulus, tensile strength, and thermomechanical parameters) and the properties of constituents (polymer matrix and reinforcement), volume fraction of components, shape and arrangement of reinforcement, and matrix-reinforcement interaction. These results can help predict and control the properties of polymer nanocomposites. Experimental results have revealed that the reinforcement size and morphology of polymer and reinforcement play a very important role in determining the performance of polymer nanocomposites. Also, the properties of polymer nanocomposites will depend on the nature of dispersion and aggregation of the reinforcements. In the polymer composite, there exists an interphase with a layer of high-density polymer around the particle. The strength of the reinforcement-matrix interaction will affect the thickness and density of the interphase. The inter-reinforcement distance and the arrangement of reinforcement are important factors to be investigated. Generally, as their size decreases and number increases, the reinforcements become closer, and the bulk properties can be modified significantly. Due to the different physical and chemical systems for different researchers, different processing

conditions are needed for different polymer systems to be formed. And it is difficult to provide one universal technique for producing polymer nanocomposites. Methods including melt mixing and in situ polymerization have been applied in the laboratory.¹

Compared with other conventional composites, the unique characteristics of polymer composite material with optimized structures are corrosion resistance, high strength-to-weight ratio, and more design flexibility. Large panels can be easily fabricated to reduce labor costs and assembly time by using polymer composites. Polymer composites can replace traditional materials, precluding the use of heavy-duty installation equipment. Unlike the traditional materials such as concrete and steel, polymer composites provide a robust alternative to the highly corrosive properties of concrete and steel. Another advantage of polymer composites is their efficient manufacturing processes; people can integrate the unique advantages of polymer matrix and reinforcement filler in the manufacturing process. According to the requirement of customers, the engineers and designers can provide high-quality, innovative, fashionable products from concept to production. The advantages of polymer composites make them highly competitive in the range of services and products for the industrial parts market, medical, architectural, building, construction, and food packaging industries.

Polymer matrix-based nanocomposites with exfoliated clay, one of the key modifications, have been reviewed [9]. In this review, the author compares properties of nanoscale dimensions to those of larger-scale dimensions. In order to get the optimized resultant nanocomposite, it is necessary to have a better understanding of the property changes as the powder (or fiber) dimensions decrease to the nanoscale level. Unlike the in situ polymerization and solution and latex methods, the melt processing technique is usually considered prior as an alternative to clays and organoclays for its economical, more flexible characteristics. As shown in Figure 1.3, immiscible (conventional or microcomposite), intercalated, and miscible or exfoliated, three different states of dispersion of organoclays in polymers, have been proposed from WAXS and TEM results. The mechanism of organoclay dispersion and exfoliation during melt processing is shown in Figure 1.4 [10].

Carbon nanotubes are ideal as advanced filler materials in polymer composites because of their good mechanical, thermal, and electronic properties. A review of the mechanical properties of carbon nanotube-polymer composites has been conducted by Coleman [11]. The progress to date in the field of mechanical reinforcement of polymers using nanotubes has been reviewed. Large aspect ratio, good dispersion, alignment, and interfacial stress transfer are important factors that affect the properties of such polymer composites. For example, the author showed that the difference between random orientation and perfect alignment is a factor of five in composite modulus. The aligned composites, especially, fiber-reinforced polymers have very anisotropic mechanical properties. If one wants to avoid the

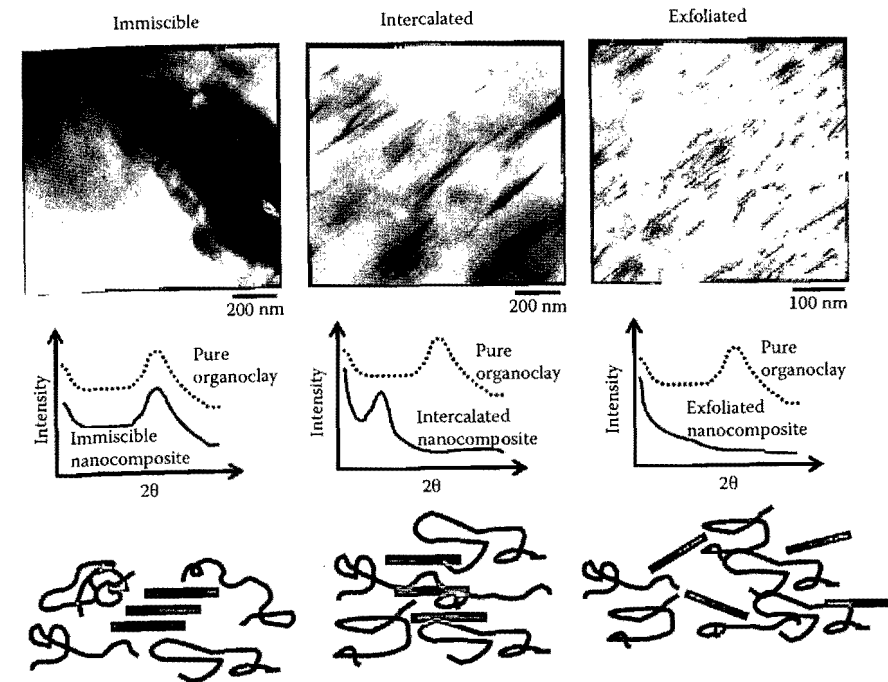


FIGURE 1.3 Illustration of different states of dispersion of organoclays in polymers with corresponding WAXS and TEM results. (Reprinted with permission from Paul, D. R. and Robeson, L. M., *Polymer*, 2008, 49, 3187–3204. Copyright 2008 Elsevier B.V.)

anisotropic properties in bulk samples, one can align the fibers randomly. In carbon nanotube-polymer composites, only the external stresses applied to the composite are transferred to the nanotube; the composite can show its excellent loadability. The interaction between polymer and nanotube in the vicinity of the interface is an important issue to investigate. Research results have indicated that interfacial interactions with nanotubes lead to an interfacial region of polymer with morphology and properties different from the bulk. The SEM images of composite fibers containing carbon nanotubes are shown in Figure 1.5 [12].

Conductive polymer is one important class of organic polymers that can conduct electricity. Inorganic nanoparticles of different nature and size were embedded into conducting polymers to endow such nanocomposites with further interesting physical properties and important application potential. A review of conducting polymer nanocomposites is given by Amitabha De [13]. Depending on the preparation methods and the nature of the inorganic materials, the properties of the resulting composite can be controlled. The TEM of a dilute dispersion of a PPy-silica colloidal nanocomposite is displayed in Figure 1.6 [14].

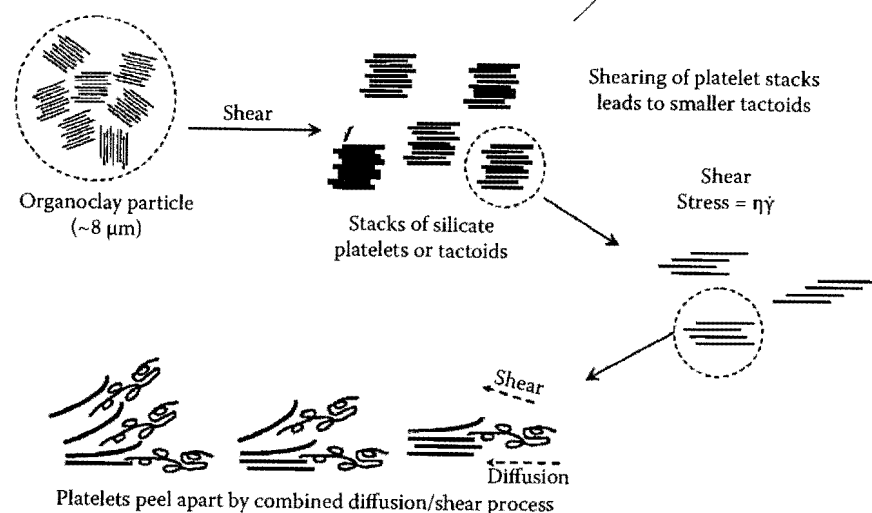


FIGURE 1.4

Mechanism of organoclay dispersion and exfoliation during melt processing. (Reprinted with permission from Fornes, T. D. et al., *Polymer* 2001, 42, 9929. Copyright 2001 Elsevier B.V.)

Poly (ethylene oxide) (PEO)-based composite polymer electrolytes have been widely investigated, and a review of PEO-based composite polymer electrolytes can be found in Reference [15]. In this paper, the author not only focuses on the experimental work but also summarizes the theoretical models for ion transport in such composite polymer electrolytes. Two different systems called *blend-based* and *mixed-phase* composite electrolytes are proposed. Blend-based systems are obtained from homogeneous solutions of two components in an appropriate common solvent. Mixed-phase systems mean that the polymer and inorganic or organic additives, not dissolved in a common solvent, are mixed inhomogeneously. In PEO-based composite polymer electrolytes, inorganic nanoparticles ZnO, LiAlO₂, or zeolites are combined with poly (ethylene oxide) to improve the mechanical properties, conductivity, and the interfacial stability. Also, the organic entities are added in the system to modify the structure of PEO, and this idea focuses on the two following research subjects: (1) synthesis of PEO-based flexible networks and (2) synthesis of composites by the addition of organic fillers [15]. Polystyrenes, polymethylmethacrylate, polyacrylamides, and polyacrylates are added to the PEO-based composite polymer electrolytes, and their effect on the conductivity is studied. Poly(ethylene glycol methylether) (PEGME) molecules modified on SnO₂ nanoparticle surfaces through exchange reactions are managed to obtain PEGME-SnO₂ stable colloids, and the PEGME-SnO₂ composites themselves are able to dissolve lithium salts to form a new type of solid polymer electrolyte. PEGME-SnO₂ stable colloids also can be used as fillers for prototypical PEO-based electrolytes, where they exhibit advantages of both organic plasticizers and inorganic

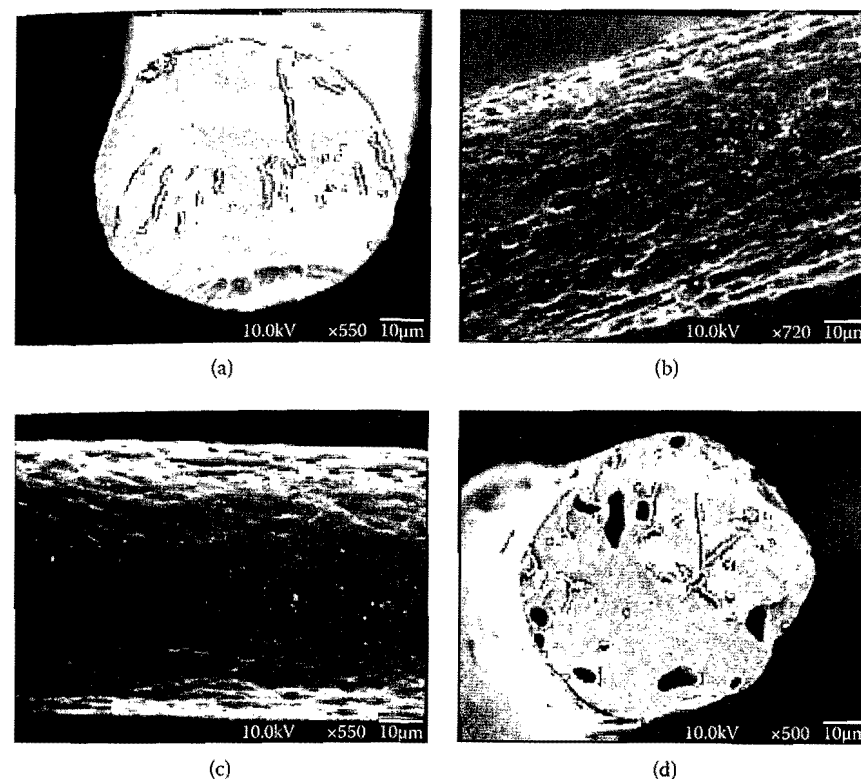


FIGURE 1.5

SEM images of composite fibers containing (a) carbon nanofibers, (b) entangled MWNT, (c) aligned MWNT, and (d) arc-MWNT. (Reprinted with permission from Sandler, J. K. et al. *Polymer* 2004, 45, 2001–2015. Copyright 2004 Elsevier B.V.)

fillers [16]. Transmission electron micrographs of the PEGME-SnO₂ nanoparticles are shown in Figure 1.7.

Polymer materials can be used in biological research and applications [17,18]. Biodegradable polymers and bioactive ceramics can be combined to form composite materials for tissue engineering scaffolds. Bioactive ceramics refer to alumina, titania, zirconia, bioglass, hydroxyapatite, etc. Also, some metals and alloys, including gold, stainless steel, and NiTi shape memory alloys can be used as biomaterials. Low biological compatibility and corrosion of metal, brittleness, high density, and low fracture strength of ceramics make polymers such as polyethylene, polyacetal, and the corresponding polymer composites excellent candidates for use in biological applications. Figure 1.8 lists the various applications of different polymer composite materials. In living systems, the responses of the host to the polymer materials can make a big difference; some polymer materials can be accepted by the body and others cannot. Great work has led to considerable progress in understanding

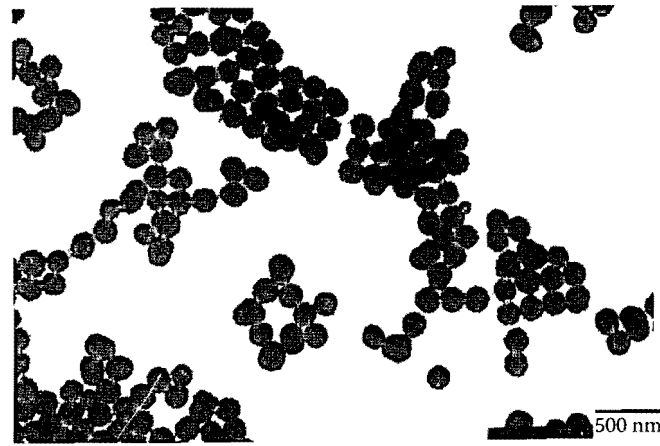


FIGURE 1.6
Transmission electron micrograph of a dilute dispersion of a PPy-silica colloidal nanocomposite. (Reproduced with permission from Butterworth, M. D. et al., *J. Colloid Interface Sci.* 1995, 174, 510. Copyright 1995 Academic Press.)

the interactions between the tissues and the materials. For the application of polymer biocomposites, the first thing to be considered is their safety and compatibility with living systems. Compatibility implies surface and structural harmony between the tissues and the polymer materials. Surface compatibility implies that researchers must take surface morphology into account, as also the physical and chemical suitability of the surface of the implant to the tissue. Structural compatibility reflects optical adaptation of the mechanical performance of the implant, including strength and effective loadability. Thus, only the ideal interfacial interaction is reached, and the

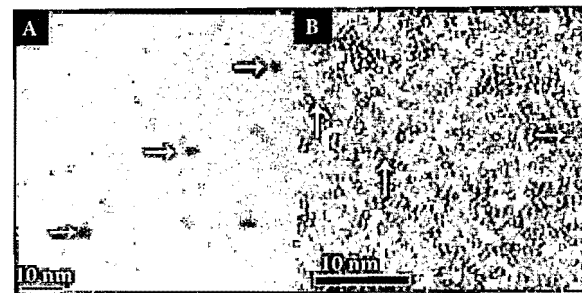
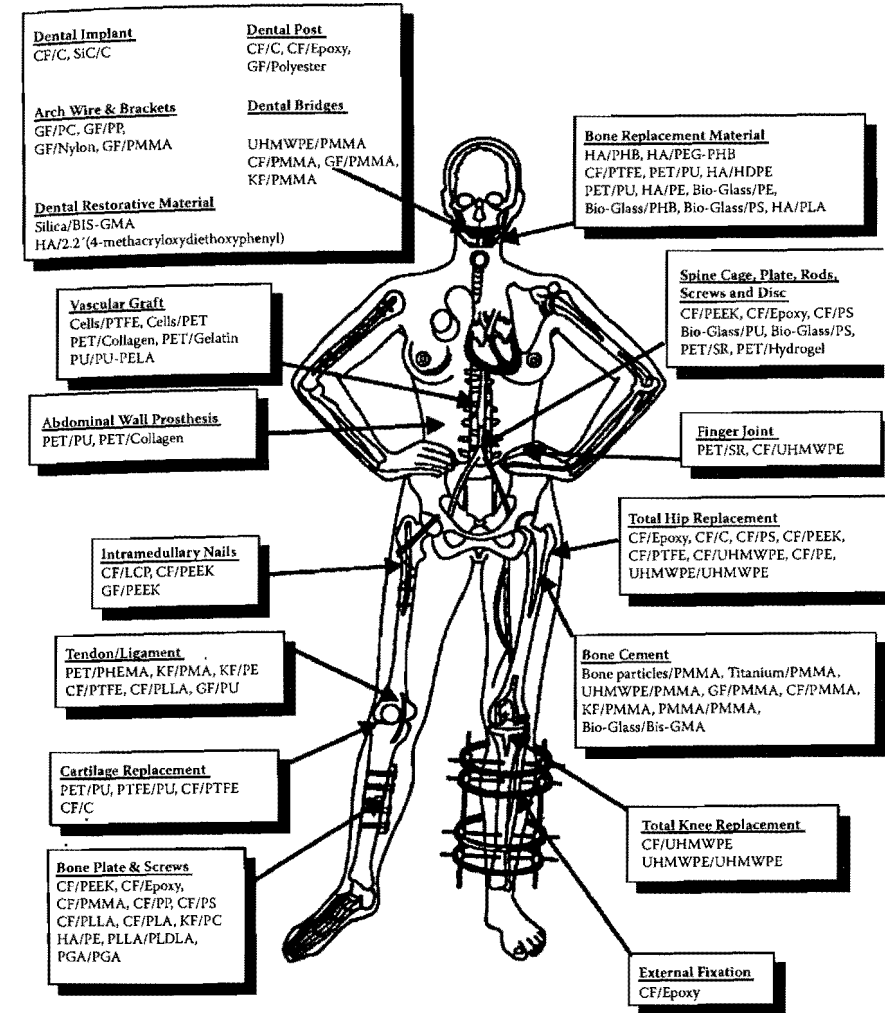


FIGURE 1.7
Transmission electron micrographs of the PEGME-SnO₂ nanoparticles (marked by arrows). A shows that nanoparticles are uniform, monodispersed and about 3 nm in diameter, while B, with a higher magnification, illustrates the crystalline phases of the nanoparticles. (Reproduced with permission from Xiong, H. et al., *J. Mater. Chem.*, 2004, 14, 2775-2780. Copyright 2004 Royal Society of Chemistry.)



CF: carbon fibers, C: carbon, GF: glass fibers, KF: kevlar fibers, PMMA: polymethylmethacrylate, PS: polysulfone, PP: polypropylene, UHMWPE: ultra-high-molecular weight polyethylene, PLDLA: poly(L-DL-lactide), PLLA: poly(L-DL-lactide), PGA: polyglycolic acid, PC: polycarbonate, PEEK: polyetheretherketone, HA: hydroxyapatite, PMA: polymethylacrylate, BIS-GMA: bis-phenol A glycidyl methacrylate, PU: polyurethane, PTEF: polytetrafluoroethylene, PET: polyethyleneterephthalate, PEA: polyethylacrylate, SR: silicone rubber, PELA: block co-polymer of lactic acid and polyethylene glycol, LCP: liquid crystalline polymer, PHB: polyhydroxybutyrate, PEG: polyethyleneglycol, PHEMA: poly(20-hydroxyethyl methacrylate)

FIGURE 1.8
Various applications of different polymer composite materials. (Reproduced with permission from Ramakrishna, S. et al., *Compos. Sci. Technol.*, 2001, 61, 1189-1224. Copyright 2001 Elsevier B.V.)

harmony between the tissues and implants made from the polymer materials can be satisfied.

The phrase *low carbon economy* now becomes synonymous with "warm gas," and solar energy is the best renewable energy. The solar cell is a device that can convert the energy of sunlight directly into electricity by the photovoltaic effect. Assemblies of solar cells are used to make solar panels, solar modules, and photovoltaic arrays that can be widely used in industry. Organic solar cells, known as *excitonic solar cells*, belong to the class of photovoltaic cells. Recently, a review of organic photovoltaics based on polymer-fullerene composite solar cells was published. The schematic illustration of a polymer-fullerene BHJ solar cell is presented in Figure 1.9. Such polymer-based photovoltaics can be processed in solution, and they have the features of low cost, low weight, and greater flexibility. Scientists now have a much better understanding of the complex interplay between the electronic and physical interactions of the polymer, and the fullerene component can assist in the design of the next generation of optimized organic solar cells [19].

Shape memory polymers (SMPs) are able to recover their original shape upon exposure to an external stimulus [20,21]. SMPs can be activated not only by heat and magnetism (similar to shape memory alloys [SMAs]) but also by light and moisture and even by a change of pH value. Thermoresponsive, light-responsive, and chemical-responsive SMPs were researched recently, although with a focus on thermoresponsive SMPs because they are better developed at present. In addition, based on the shape memory effect, some novel multifunctional SMPs or nano SMP composites have also been proposed.

1.6 Fabrication of Polymer Nanocomposite

It is a challenge to fabricate polymer matrix nanocomposites with good performance. Several processing techniques including melt mixing and in situ polymerization have been applied in the laboratory. Melt mixing as a method of dispersing carbon nanotubes into thermoplastic polymers is discussed in the reference [22]. The author provides two ways of introducing nanotubes into polymer matrices. In the first case, commercially available master batches of nanotube or polymer composites are diluted by the pure polymer in a subsequent melt mixing process (master batch method), which means that the starting materials are already preformed polymer composites. However, in the other case, nanotubes as reinforcement and polymer as matrix are used as the starting materials, then nanotube reinforcement is directly incorporated into the polymer matrix. The results show that the master batch method is applicable and easily accessible for small- and medium-sized enterprises. And the percolation only slightly depends upon the mixing equipment and the processing conditions. In the direct incorporation method, the electrical

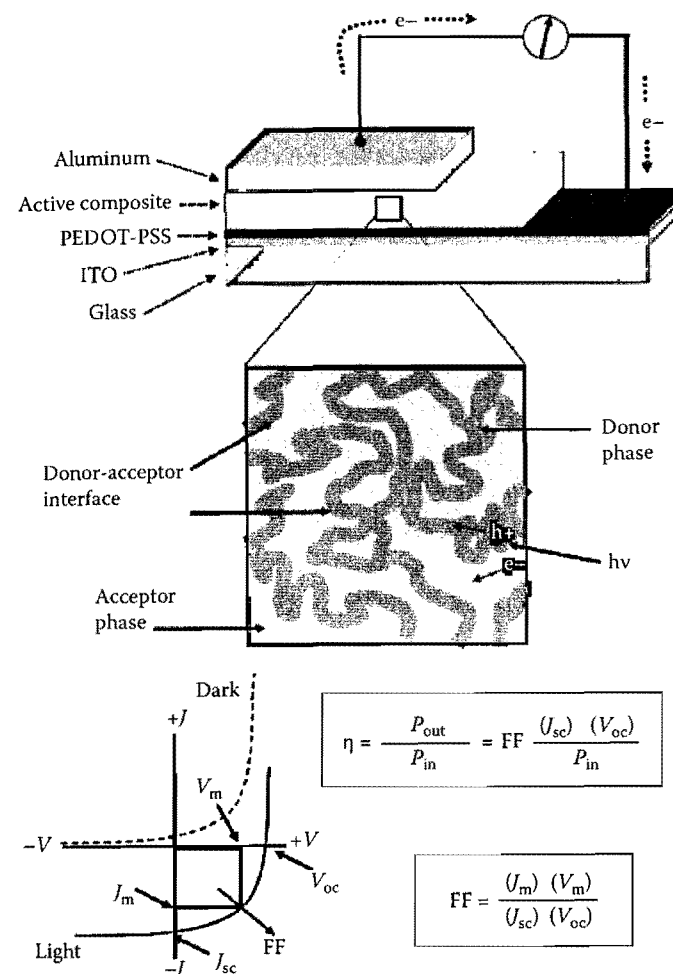


FIGURE 1.9

Schematic illustration of a polymer-fullerene BHJ solar cell, with a magnified area showing the bicontinuous morphology of the active layer. ITO is indium tin oxide, and PEDOT-PSS is poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate. The typical current-voltage characteristics for dark and light current in a solar cell illustrate the important parameters for such devices: J_{sc} is the short-circuit current density, V_{oc} is the open circuit voltage, J_m and V_m are the current and voltage at the maximum power point, and FF is the fill factor. The efficiency (η) is defined, both simplistically as the ratio of power out (P_{out}) to power in (P_{in}), as well as in terms of the relevant parameters derived from the current-voltage relationship. (Reproduced with permission from Thompson, B. C. and Frechet, J. M. J., *Angew. Chem. Int. Ed.* 2008, 47, 58-77. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.)

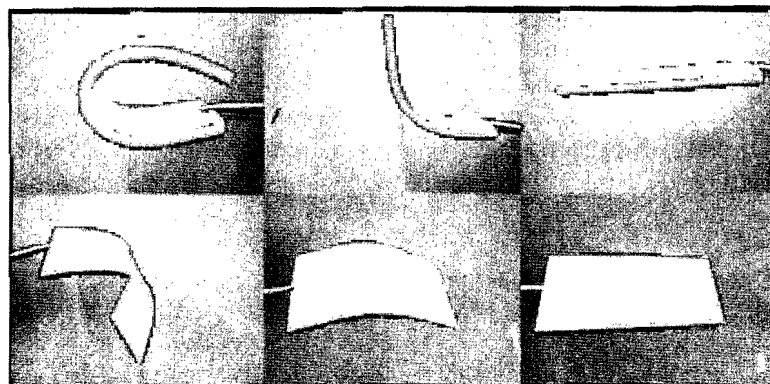


FIGURE 1.10 Time series photographs that show the recovery of a pure SMP (top row) and a glass fiber-reinforced SMP (bottom row).

properties of composites prepared will be determined by the kind of the nanotubes, different sizes, purity, and defect levels, even the purification and modification steps [22]. In polymer chemistry, *in situ* means "in the polymerization mixture." The *in situ* polymerization is an effective method applied to prepare polymer nanocomposite material. In this method, the nanoreinforcement is fixed with a structure that is impregnated with a monomer and the monomer polymerized. Usually, the monomer is very fluid and will not disturb the nanoreinforcement arrangement. After polymerization, the polymer nanocomposite material is obtained. The *in situ* polymerization method has the advantage of dispersing nanofillers effectively in monomeric liquids and consequently in the polymer nanocomposite.

Open (closed) mold processes; filament winding, and pultrusion processes are the main methods of fabricating polymer nanocomposites in industry. Molding is the process of manufacturing the pliable raw material using a rigid frame or model. In open-mold processes, a single positive or negative mold surface is used to produce laminated fiber-reinforced polymer structures, and the starting materials (resins, fibers, etc.) are applied to the mold in layers, building up to the desired thickness. Then, curing and part removal follow until the final product is finished. Compared with the open-mold processes, the tooling cost of closed-mold processes is more than double due to the more complex equipment required. However, closed-mold processes have the following advantages: good finish on surfaces, higher production rates, closer control over tolerances, and more complex three-dimensional shapes. In the filament winding technique, the mandrel rotates, while a carriage moves horizontally, laying down nanofibers in the desired pattern. For example, the glass or carbon nanofibers are coated with resin as they are wound. After reaching the desired thickness, the mandrel is put in an oven for resin solidification. Finally, the mandrel is removed,

and we get the hollow final product. Pultrusion is a manufacturing process for producing continuous lengths of reinforced polymer structural shapes with constant cross sections. The starting materials can be liquid resin mixtures and flexible reinforcement fibers. This process involves pulling the resin matrix and the reinforcement fiber through a heated steel-forming die, where the resin undergoes polymerization. The reinforcement materials are in continuous forms, and the cured profile is formed based on the shape of the die.

While the polymer matrix and the reinforcement are being combined, the starting materials may be kept as separate entities when they arrive at the fabrication operation. Then, the polymer matrix and the reinforcement are combined into the composite during shaping. Also, the polymer matrix and the reinforcement can be combined into some starting form that is convenient for use in the shaping process. In future, research activity in industry will focus on the optimization of polymer composite formulations, optimization of polymer composite forming processes, improvement of polymer composites performance, and reduction of the cost.

1.7 Future Trends

There have been many achievements in the field of polymer nanocomposite technology. We can easily see the potential for applications of polymer nanocomposites in the civil and military fields. For example, polymer nanocomposites have emerged as an attractive material in construction, aerospace, biomedical, marine, electronics, and recreation industries for their excellent properties. Great efforts have been undertaken to modify these materials at the nanoscale to optimize their performance. Carbon nanotube-reinforced nanocomposites, multifunctional polymeric smart materials, and new functional polymer nanocomposites are being explored for unusual behaviors in order to fulfill more than one task in automotive, biological, aerospace, marine, manufacturing, and defense technologies. It is believed that multifunctional polymer nanocomposites will dominate our lives in future.

References

1. Iijima, S., *Nature*, 1991, 354, 56–58.
2. Hodak, J. H., Henglein, A., Hartland, G. V., *J. Phys. Chem. B*, 2000, 104, 9954.
3. Peng, Z. A., Peng, X., *J. Am. Chem. Soc.*, 2001, 123, 1389.
4. Carpenter, E. E., Ph.D. thesis, University of New Orleans, New Orleans, LA, 1999.
5. Katz, E., Willner, I., *Angew. Chem. Int. Ed.*, 2004, 43, 6042–6108.

6. Trindade, T., O'Brien, P., Pickett, N. L., *Chem. Mater.*, 2001, 13, 3843–3858.
7. Fendler, J. H., *Chem. Mater.*, 1996, 8, 1616–1624.
8. Cushing, B. L., Kolesnichenko, V. L., O'Connor, C. J., *Chem. Rev.*, 2004, 104, 3893–3946.
9. Paul, D. R., Robeson, L. M., *Polymer*, 2008, 49, 3187–3204.
10. Fornes, T. D., Yoon, P. J., Keskkula, H., Paul, D. R., *Polymer* 2001, 42, 9929.
11. Coleman, J. N., Khan, U., Blau, W. J., Gun'ko, Y. K., *Carbon* 2006, 44, 1624–1652.
12. Sandler, J. K. W., Pegel, S., Cadek, M., Gojny, F., van Es, M., Lohmar, J. et al. *Polymer* 2004, 45, 2001–2015.
13. Gangopadhyay, R., De, A., *Chem. Mater.* 2000, 12, 608.
14. Butterworth, M. D., Corradi, R., Johal, J., Lascelles, S. F., Maeda, S., Armes, S. P., *J. Colloid Interface Sci.* 1995, 174, 510.
15. Quartarone, E., Mustarelli, P., Magistris, A., *Solid State Ionics* 1998, 110, 1–14.
16. Xiong, H., Liu, D., Zhang, H., Chen, J., *J. Mater. Chem.*, 2004, 14, 2775–2780.
17. Ramakrishna, S., Mayer, J., Wintermantel, E., Leong, K. W., *Compos. Sci. Technol.*, 2001, 61, 1189–1224.
18. Rezwani, K., Chen, Q. Z., Blaker, J. J., Aldo Roberto Boccaccini, *Biomaterials* 2006, 27, 3413–3431.
19. Thompson, B. C., Frechet, J. M. J., *Angew. Chem. Int. Ed.* 2008, 47, 58–77.
20. Behl, M., Lendlein, A., *Mater. Today* 2007, 10, 20–28.
21. Leng, J. S., Lv, H. B., Liu, Y. J., Huang, W. M., Du, S. Y., *MRS Bulletin.* 2009, 34, 848–855.
22. Pötschke, P., Bhattacharyya, A. R., Janke, A., Pegel, S., Leonhardt, A., Täschner, C., Ritschel, M., Roth, S., Hornbostel, B., Cech, J., *Fullerenes, Nanotubes, Carbon Nanostruc.*, 2005, 13, 211–224.