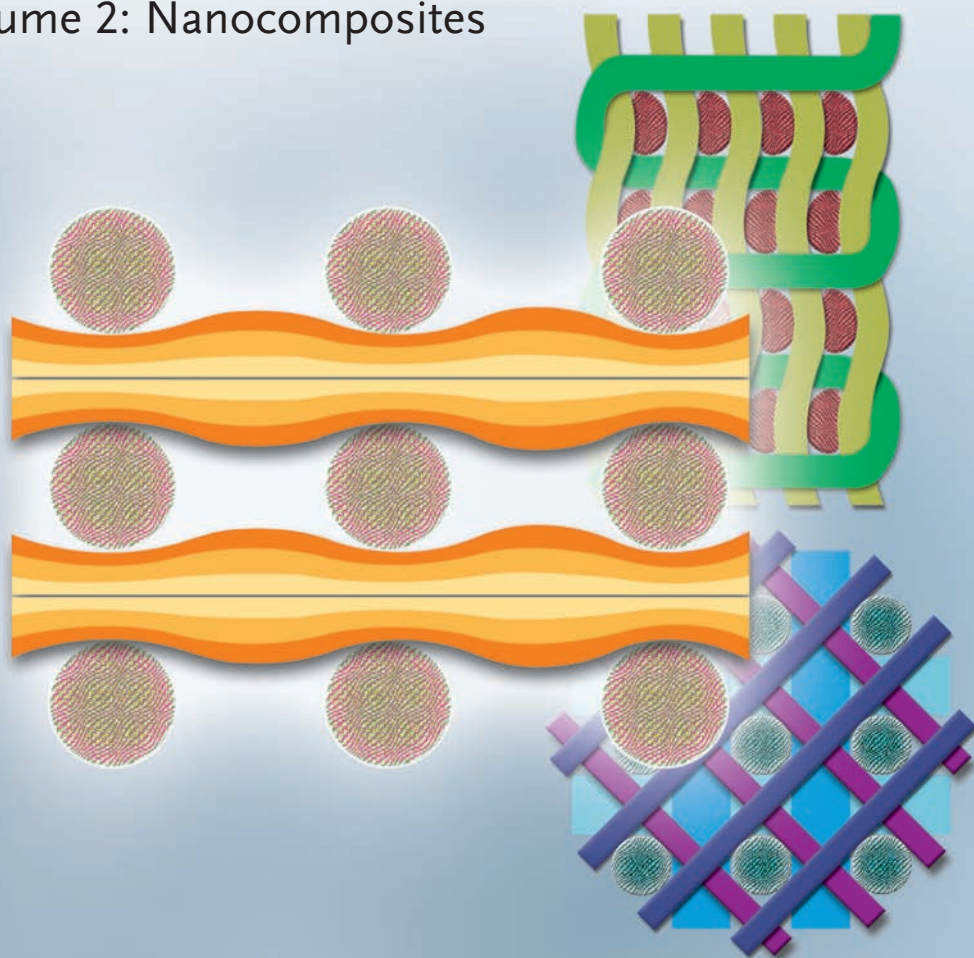


Edited by Sabu Thomas, Kuruvilla Joseph,  
S. K. Malhotra, Koichi Goda, M. S. Sreekala

 WILEY-VCH

# Polymer Composites

Volume 2: Nanocomposites





*Edited by*  
*Sabu Thomas, Kuruvilla Joseph,*  
*Sant Kumar Malhotra, Koichi Goda,*  
*and Meyyarappallil Sadasivan Sreekala*

**Polymer Composites**

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*Edited by Sabu Thomas, Kuruvilla Joseph,  
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## **Polymer Composites**

Volume 2



WILEY-VCH Verlag GmbH & Co. KGaA

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**Library of Congress Card No.:** applied for

### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

### **Bibliographic information published by the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA,  
Boschstr. 12, 69469 Weinheim, Germany

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**Print ISBN:** 978-3-527-32979-3

**ePDF ISBN:** 978-3-527-65240-2

**ePub ISBN:** 978-3-527-65239-6

**mobi ISBN:** 978-3-527-65238-9

**oBook ISBN:** 978-3-527-65237-2

**Composition** Thomson Digital, Noida, India

**Printing and Binding** Markono Print Media Pte Ltd,  
Singapore

**Cover Design** Adam Design, Weinheim

Printed in Singapore

Printed on acid-free paper

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## 1

**State of the Art – Nanomechanics**

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## 1.1

**Introduction**

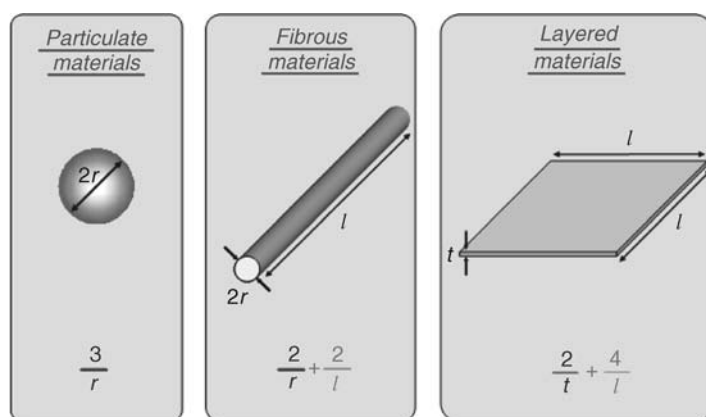
*Nanomechanics*, a branch of *nanoscience*, focuses on the fundamental *mechanical* properties of physical systems at the nanometer scale. It has emerged on the crossroads of classical mechanics, solid-state physics, statistical mechanics, materials science, and quantum chemistry. Moreover, it provides a scientific foundation for *nanotechnology*. Often, it is looked upon as a *branch* of nanotechnology, that is, an applied area with a focus on the mechanical properties of *engineered* nanostructures and nanosystems that include nanoparticles, nanopowders, nanowires, nanorods, nanoribbons, nanotubes, including carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), nanoshells, nanomembranes, nanocoatings, nanocomposites, and so on.

Nanotechnology can be broadly defined as “The creation, processing, characterization, and utilization of materials, devices, and systems with dimensions on the order of 0.1–100 nm, exhibiting novel and significantly enhanced physical, chemical, and biological properties, functions, phenomena, and processes due to their nanoscale size” [1]. Nanobiotechnology, nanosystems, nanoelectronics, and nanostructured materials, especially nanocomposites, are of current interest in nanotechnology. Polymer nanocomposites have gained attention as a means of improving polymer properties and extending their utility by using molecular or nanoscale reinforcements rather than conventional particulate fillers. The transition from microparticles to nanoparticles yields dramatic changes in physical properties.

Recently, the advances in synthesis techniques and the ability to characterize materials on atomic scale have led to a growing interest in nanosized materials. The invention of nylon 6/clay nanocomposites by the Toyota Research Group of Japan heralded a new chapter in the field of polymer composites. Polymer nanocomposites combine these two concepts, that is, composites and nanosized materials. Polymer nanocomposites are materials containing inorganic components that have dimensions in nanometers. In this chapter, the discussion is restricted to polymer

nanocomposites made by dispersing two-dimensional layered nanoclays as well as nanoparticles into polymer matrices. In contrast to the traditional fillers, nanofillers are found to be effective even at as low as 5 wt% loading. Nanosized clays have dramatically higher surface area compared to their macrosized counterparts such as china clay or talc. This allows them to interact effectively with the polymer matrix even at lower concentrations. As a result, polymer–nanoclay composites show significantly higher modulus, thermal stability, and barrier properties without much increase in the specific gravity and sometimes retaining the optical clarity to a great extent. As a result, the composites made by mixing layered nanoclays in polymer matrices are attracting increasing attention commercially. Thus, the understanding of the links between the microstructure, the flow properties of the melt, and the solid-state properties is critical for the successful development of polymer–nanoclay composite products.

Nevertheless, these promising materials exhibit behavior different from conventional composite materials with microscale structure due to the small size of the structural unit and high surface area/volume ratio. Nanoscale science and technology research is progressing with the use of a combination of atomic scale characterization and detailed modeling [2]. In the early 1990s, Toyota Central Research Laboratories in Japan reported work on a nylon 6 nanocomposite [3], for which a very small amount of nanofiller loading resulted in a pronounced improvement in thermal and mechanical properties. Common particle geometries and their respective surface area/volume ratios are shown in Figure 1.1. For the fiber and the layered material, the surface area/volume ratio is dominated, especially for nanomaterials, by the first term in the equation. The second term ( $2/l$  and  $4/l$ ) has a very small influence (and is often omitted) compared to the first term. Therefore, logically, a change in particle diameter, layer thickness, or fibrous material diameter from the micrometer to nanometer range will affect the surface area/volume ratio by three orders of magnitude [4]. Typical nanomaterials currently under investigation include



**Figure 1.1** Common particle reinforcements and their respective surface area/volume ratios [4].

nanoparticles, nanotubes, nanofibers, fullerenes, and nanowires. In general, these materials are classified by their geometries; broadly, the three classes are particle, layered, and fibrous materials [4,5]. Carbon black, silica nanoparticles, and polyhedral oligomeric silsesquioxanes (POSS) can be classified as nanoparticle reinforcing agents while nanofibers and carbon nanotubes are examples of fibrous materials [5]. When the filler has a nanometer thickness and a high aspect ratio (30–1000) plate-like structure, it is classified as a layered nanomaterial (such as an organo-silicate) [6]. The change of length scales from meters (finished woven composite parts), micrometers (fiber diameter), and submicrometers (fiber/matrix interphase) to nanometers (nanotube diameter) presents tremendous opportunities for innovative approaches in the processing, characterization, and analysis/modeling of this new generation of composite materials. As scientists and engineers seek to make practical materials and devices from nanostructures, a thorough understanding of the material behavior across length scales from the atomistic to macroscopic levels is required. Knowledge of how the nanoscale structure influences the bulk properties will enable design of the nanostructure to create multifunctional composites.

Wang *et al.* synthesized poly(styrene–maleic anhydride) (PSMA)/TiO<sub>2</sub> nanocomposites via the hydrolysis and condensation reactions of multicomponent sol since the PSMA has functional groups that can anchor TiO<sub>2</sub> and prevent it from aggregating [7]. Polystyrene or polycarbonate rutile nanocomposites have been synthesized by Nussbaumer *et al.* [8]. Singh *et al.* [9] studied the variation in fracture toughness of polyester resin due to the addition of aluminum particles of 20, 3.5, and 100 nm diameter. Results indicate an initial enhancement in fracture toughness followed by decrease at higher particle volume fraction. This phenomenon is attributed to the agglomeration of nanoparticles at higher particle volume content. Lopez *et al.* [10] examined the elastic modulus and strength of vinyl ester composites after the addition of 1, 2, and 3 wt% of alumina particles of 40 nm, 1  $\mu$ m, and 3  $\mu$ m size. For all particle sizes, the composite modulus increases monotonically with particle weight fraction. However, the strengths of composites are all below the strength of neat resin due to nonuniform particle size distribution and particle aggregation. The mechanical behavior of alumina-reinforced poly(methyl methacrylate) (PMMA) composites was studied by Ash *et al.* [11].

## 1.2

### Nanoplatelet-Reinforced Composites

In the case of layered silicates, the filler is present in the form of sheets one to a few nanometer thick and hundreds to thousands nanometer long. In general, the organically modified silicate nanolayers are referred to as “nanoclays” or “organo-silicates” [12]. It is important to know that the physical mixture of a polymer and layered silicate may not form nanocomposites [13]. Pristine-layered silicates usually contain hydrated Na<sup>+</sup> or K<sup>+</sup> ions [13]. To render layered silicates miscible with other polymer matrices, it is required to convert the normally hydrophilic silicate surface into an organophilic one, which can be carried out by ion-exchange reactions with

cationic surfactants [13]. Sodium montmorillonite ( $\text{Na-MMT}$ ,  $\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot m\text{H}_2\text{O}$ )-type layered silicate clays are available as micron-sized tactoids, which consist of several hundred individual plate-like structures with dimensions of  $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m} \times 1\text{ nm}$ . These are held together by electrostatic forces (the gap in between two adjacent particles is  $0.3\text{ nm}$ ). The MMT particles, which are not separated, are often referred to as tactoids. The most difficult task is to break down the tactoids to the scale of individual particles in the dispersion process to form true nanocomposites, which has been a critical issue in current research [14,15–24]. Natural flake graphite (NFG) is also composed of layered nanosheets [25], where carbon atoms positioned on the NFG layer are tightened by covalent bonds, while those positioned in adjacent planes are bound by much weaker van der Waals forces. The weak interplanar forces allow for certain atoms, molecules, and ions to intercalate into the interplanar spaces of the graphite. The interplanar spacing is thus increased [25]. As it does not bear any net charge, intercalation of graphite cannot be carried out by ion-exchange reactions in the galleries like layered silicates [25]. The original graphite flakes with a thickness of  $0.4\text{--}60\text{ nm}$  may expand up to  $2\text{--}20\text{ }\mu\text{m}$  in length [26]. These sheets/layers get separated down to  $1\text{ nm}$  thickness, forming high aspect ratio ( $200\text{--}1500$ ) and high modulus ( $\sim 1\text{ TPa}$ ) graphite nanosheets. Furthermore, when dispersed in the matrix, the nanosheet exposes an enormous interface surface area ( $2630\text{ m}^2/\text{g}$ ) and plays a key role in the improvement of both the physical and mechanical properties of the resultant nanocomposite [27]. The various preparative techniques for this type of nanocomposites are discussed below.

### 1.3

#### Exfoliation–Adsorption

This technique is based on a solvent system in which the polymer or prepolymer is soluble and the silicate layers are swellable. The layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent such as water, acetone, chloroform, or toluene. When the polymer and the layered silicate are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. The solvent is evaporated and the intercalated structure remains. For the overall process, in which polymer is exchanged with the previously intercalated solvent in the gallery, a negative variation in Gibbs free energy is required. The driving force for polymer intercalation into layered silicate from solution is the entropy gained by desorption of solvent molecules, which compensates for the decreased entropy of the intercalated chains. This method is good for the intercalation of polymers with little or no polarity into layered structures and facilitates production of thin films with polymer-oriented clay intercalated layers. The major disadvantage of this technique is the nonavailability of compatible polymer–clay systems. Moreover, this method involves the copious use of organic solvents, which is environmentally unfriendly and economically prohibitive. Biomedical poly(urethane–urea) (PUU)/MMT (MMT modified with

dimethyl ditallow ammonium cation) nanocomposites were prepared by adding OMLS (organically modified layered silicate) suspended in toluene dropwise to the solution of PUU in *N,N*-dimethylacetamide (DMAC). The mixture was then stirred overnight at room temperature, the solution was degassed, and the films were cast on round glass Petri dishes. The films were air dried for 24 h, and subsequently dried under vacuum at 50 °C for 24 h. Wide-angle X-ray diffraction (WAXD) analysis indicated the formation of intercalated nanocomposites [28]. The effects of heat and pressure on microstructures of isobutylene–isoprene rubber/clay nanocomposites prepared by solution intercalation (S-IIRCNS) were investigated [29]. A comparison of the WAXD patterns of untreated S-IIRCNS and nanocomposites prepared by melt intercalation (M-IIRCNS) reveals that the basal spacing of the intercalated structures in untreated M-IIRCNS (i.e., 5.87 nm) is much larger than that in S-IIRCNS (i.e., 3.50 nm), which is likely a result of the different methods of preparation. Tolle and Anderson [30] investigated the sensitivity of exfoliation for processing. They found that both lower temperatures for isothermal curing and higher heating rates for nonisothermal curing cause an inhibition of exfoliated morphology. There are several reports regarding the preparation of nanocomposites using the solvents [31–36]. Kornmann *et al.* [37] investigated the effect of three different curing agents upon the organoclay exfoliation in the diglycidyl ether of bisphenol A (DGEBA)-based system. In their work, exfoliation of organoclay occurred in cycloaliphatic diamine-cured DGEBA nanocomposites only at higher temperatures. Messermith and Giannelis [38] prepared exfoliated layered silicate epoxy nanocomposites from DGEBA and a nadic methyl anhydride curing agent and found that the dynamic storage modulus improved. The Toyota Research Group has been the first to use this method to produce polyimide (PI) nanocomposites [39,40]. Du *et al.* [41] prepared expandable polyaniline/graphite nanocomposites by chemical and physical treatments, especially by microwave irradiation. Instead of the usual  $\text{HNO}_3\text{--H}_2\text{SO}_4$  route, they prepared the nanocomposites through the  $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$  route to avoid the evolution of poisonous  $\text{NO}_x$ . Shioyama [42] reported improved exfoliation at weight fractions of graphite below 1 wt% through polymerization with vaporized monomers such as styrene and isoprene. Fukushima and Drazal [43] used  $\text{O}_2$  plasma-treated graphite nanoplatelets in an acrylamide/benzene solution. Improved mechanical and electrical properties were achieved using this technique. In the case of graphite, the term “complete exfoliation” has no exact meaning. It does not mean a single layer sheet as in the case of polymer–clay nanocomposites; it may mean a separated graphite flake that is completely delaminated layer by layer.

## 1.4

### **In Situ Intercalative Polymerization Method**

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution, so the formation cannot occur between the intercalated sheets. Polymerization can be initiated by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside

the interlayer before the swelling step. Yao *et al.* [44] reported the preparation of a novel kind of PU/MMT nanocomposite using a mixture of modified 4,4'-diphenylmethane diisocyanate (MMDI), modified polyether polyol (MPP), and Na-MMT. In a typical synthetic route, a known amount of Na-MMT was first mixed with 100 ml of MPP and then stirred at 50 °C for 72 h. Then, the mixture of MPP and Na-MMT was blended with a known amount of MMDI and stirred for 30 s at 20 °C, and finally cured at 78 °C for 168 h. Wang and Pinnavaia [45] reported the preparation of polyurethane–MMT nanocomposites using this technique. It can be seen that the extent of gallery expansion is mainly determined by the chain length of the gallery onium ions and is independent of the functionality or molecular weight of the polyols and the charge density of the clay. These nanocomposites exhibit an improvement in elasticity, as well as in modulus. In another study, Pinnavaia and Lan [46] reported the preparation of nanocomposites with a rubber/epoxy matrix obtained from DGEBA derivatives cured with a diamine so as to reach subambient glass transition temperatures. It has been shown that depending on the alkyl chain length of modified MMT, an intercalated and partially exfoliated or a totally exfoliated nanocomposite can be obtained.

## 1.5

### Melt Intercalation

Recently, the melt intercalation technique has become the standard for the preparation of polymer nanocomposites. During polymer intercalation from solution, a relatively large number of solvent molecules have to be desorbed from the host to accommodate the incoming polymer chains. The desorbed solvent molecules gain one translational degree of freedom, and the resulting entropic gain compensates for the decrease in conformational entropy of the confined polymer chains. There are many advantages to direct melt intercalation over solution intercalation. Direct melt intercalation is highly specific for the polymer, leading to new hybrids that were previously inaccessible. In addition, the absence of solvent makes the process economically favorable method for industries from a waste perspective. On the other hand, during this process only a slow penetration (transport) of polymer takes place within the confined gallery. Polyamide 66/SEBS-g-MA alloys and their nanocomposites were prepared by melt compounding using a twin-screw extruder. Morphological investigations with different methods show pseudo-one-phase-type morphology for these prepared alloys at all percentages of rubber. Impact and tensile test results showed that rubber-toughened samples exhibit significantly more impact strength and elongation at break compared to virgin polyamide. Samples with 20% of rubber show impact strength about 15 times and elongation at yield several times more than those of virgin polyamide. So, these rubber-modified polyamides can be considered as supertoughened rubber. A general type organoclay at 4 and 8% has been used with rubber-toughened samples to tolerate their modulus and tensile strength. Obtained results show that nanoclay could significantly increase modulus and tensile strength of rubber-modified

polyamide 66 without considerable effects on impact strength. WAXD and scanning electron microscopy (SEM) results show that the polyamide 66 nanocomposites are better exfoliated in the presence of SEBS-g-MA. The reduced modulus and strength of alloys with functional rubber addition were counteracted by incorporation of organoclay without significant negative effects on the impact strength. Comparison of mechanical properties of these rubber-toughened polyamides with virgin polyamides shows an increase of about 1200 and 240% for impact strength and elongation at break, respectively, which is a very interesting result and shows excellent toughening of polyamide 66 with SEBS-g-MA rubber [47].

## 1.6

### Nanofiber-Reinforced Composites

Vapor-grown carbon nanofibers (CNFs) have been used to reinforce a variety of polymers, including polypropylene (PP), polycarbonate, nylon, poly(ether sulfone), poly(ethylene terephthalate), poly(phenylene sulfide), acrylonitrile-butadiene-styrene (ABS), and epoxy. Carbon nanofibers are known to have wide-ranging morphologies, including structures with a disordered bamboo-like structure [48]. Finegan *et al.* [49,50] have investigated the processing and properties of carbon nanofiber/PP nanocomposites. In their work, they used a variety of as-grown nanofibers. Carbon nanofibers that were produced with longer gas-phase feedstock residence times were less graphitic but adhered better to the PP matrix, with composites showing improved tensile strength and Young's modulus. Oxidation of the carbon nanofiber was found to increase adhesion to the matrix and increase composite tensile strength, but extended oxidation deteriorated the properties of the fibers and their composites. In their investigation on the nanofiber composite damping properties, Finegan *et al.* [50] concluded that the trend of stiffness variation with fiber volume content is opposite to the trend of loss factor and damping in the composite is matrix dominated. Ma *et al.* [51] have spun polymer fibers with carbon nanofibers as reinforcement.

## 1.7

### Characterization of Polymer Nanocomposites

Characterization tools are crucial to comprehend the basic physical and chemical properties of polymer nanocomposites. The commonly used powerful techniques are WAXD, small-angle X-ray scattering (SAXS), SEM, and transmission electron microscopy (TEM). The SEM provides images of surface features associated with a sample. However, there are two other techniques, scanning probe microscopy (SPM) and scanning tunneling microscopy (STM), that are indispensable in nanotube research. The SPM uses the interaction between a sharp tip and a surface to obtain an image. In STM, a sharp conducting tip is held sufficiently close to a surface (typically about 0.5 nm) such that electrons can "tunnel" across the gap. This method provides surface structural and electronic information at atomic level. The

invention of the STM inspired the development of other “scanning probe” microscopes, such as the atomic force microscope (AFM).

Due to its simplicity and availability, WAXD is most commonly used to probe the nanocomposite structure [52–58] and occasionally to study the kinetics of the polymer melt intercalation [59]. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. For example, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Although WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1–4 nm), little can be said about the spatial distribution of the silicate layers or any structural nonhomogeneities in nanocomposites. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. However, special care must be exercised to guarantee a representative cross section of the sample. However, TEM is time intensive and gives only qualitative information on the sample as a whole, while low-angle peaks in WAXD allow quantification of changes in layer spacing.

## 1.8

### Recent Advances in Polymer Nanocomposites

The effects of the coating amount of surfactant and the particle concentration on the impact strength of PP/CaCO<sub>3</sub> nanocomposites were investigated [60]. The morphological features and the free volume properties of an acrylic resin/aponite nanocomposite are investigated using X-ray diffraction and positron annihilation lifetime spectroscopy [61]. Structure and rheological properties of hybrids with polymer matrix and layered silicates as filler were studied. The peculiarity of this study is that the matrix depending on temperature can form different phase states including liquid crystalline (LC). So, a possibility of coexistence and superposition of different ordered structures can be realized at different temperatures. Three different fillers were used, natural Na-MMT and organoclays obtained by treating MMT with surfactants varying in polarity of their molecules. Depending on the type of clay, materials with different morphologies can be obtained. X-ray data showed that polyethylene glycol (PEG) intercalates all types of clay used whereas penetration of hydroxypropyl cellulose (HPC) macromolecules into clay galleries during mixing does not occur. Clay modified with more polar surfactants should be treated as the most convenient material to be intercalated by PEG [62]. With the incorporation of less than 9 wt% nanoclay, the dynamic storage modulus above the glass transition region of such a blend increases from 2 to 54 MPa. This tremendous reinforcing as well as the compatibilization effect of the nanoclay was understood by

thermodynamically driven preferential framework-like accumulation of exfoliated nanoclay platelets in the phase border of CR and EPDM, as observed, that is, from TEM [63]. A modified method for interconnecting multiwalled carbon nanotubes (MWCNTs) was put forward. Interconnected MWCNTs were obtained by reaction of acyl chloride and amino groups. SEM shows that heterojunctions of MWCNTs with different morphologies were formed. Then specimens of pristine MWCNTs, chemically functionalized MWCNTs, and interconnected MWCNT-reinforced epoxy resin composites were fabricated by cast molding. Tensile properties and fracture surfaces of the specimens were investigated [64]. A model to simulate the conductivity of carbon nanotube/polymer nanocomposites is presented. The proposed model is based on hopping between the fillers. A parameter related to the influence of the matrix in the overall composite conductivity is defined. It is demonstrated that increasing the aspect ratio of the fillers will increase the conductivity. Finally, it is demonstrated that the alignment of the filler rods parallel to the Measurement direction results in higher conductivity values, in agreement with results from recent experimental work done by Silva and coworkers. [65]. Polybutadiene (PB)/allylisobutyl polyhedral oligomeric silsesquioxane (A-POSS) nanocomposites have been prepared by using A-POSS and butadiene (Bd) as comonomers, *n*-BuLi as initiator, cyclohexane as solvent, and ethyl tetrahydrofurfuryl ether as structure modifier through the anionic polymerization technique. The reaction conditions, the type and content of the modifier and POSS, and so on affecting the copolymerization process and the microstructure of the nanocomposites were also investigated. The results showed that POSS incorporation obviously decreased the rate of polymerization and the molecular weight of the copolymers and increased polydispersity index of the copolymers. The reaction conditions (the reaction time and reaction temperature) had little effect on copolymerization [66].

## 1.9

### Future Outlook

Biodegradable polymer-based nanocomposites have a great deal of future promise for potential applications as high-performance biodegradable materials. Scientists must continue to investigate strategies to optimize the fabrication of nanotube-enabled materials to achieve both improved mechanical and transport properties. The nanoscale of the reinforcement also presents additional challenges in mechanics research since we now must account for interactions at the atomic scale. Ultimately, a basic understanding of the structure–property relations will enable the nanoscale design of multifunctional materials for engineering applications ranging from structural and functional materials to biomaterials and beyond.

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