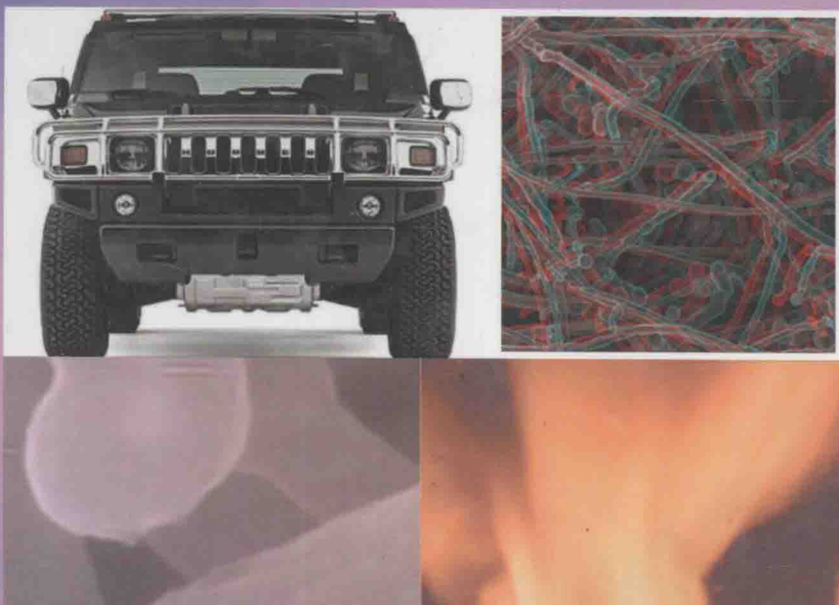
Rakesh K. Gupta, Elliot Kennel,
and Kwang-Jea Kim

Polymer Nanocomposites Handbook



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Polymer Nanocomposites

Handbook

Dedication

For my wife, Gunjan, and for our daughters, Deepti and Neha.

Rakesh K. Gupta

To the memory of Rick Smalley, Roger Bacon, Leonard Singer, and the other pioneers of nanomaterial development, without whom carbon nanocomposites would not exist; and to Max Lake who got us started on nanomaterials in the first place in 1985.

Elliot Kennel

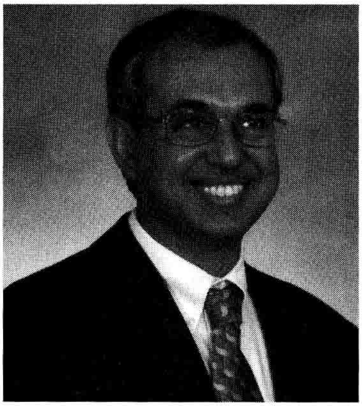
For my wife, Hyekyong, and for my daughter, Carol Tongyon.

Kwang-Jea Kim

The universe is created by the association of "DRAVYA," an ultrafine entity from which matter, energy, time, directions and mind emanate.

—Maharishi Kannad
Vaishesik Darshan
written around 2000 B.C.

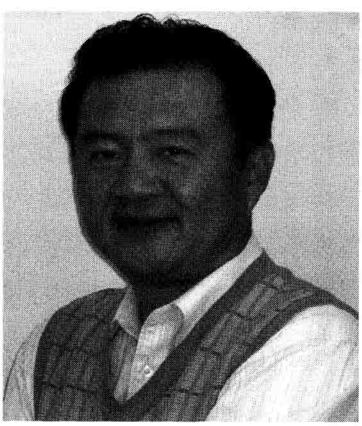
About the Editors



Rakesh K. Gupta has been teaching at West Virginia University (WVU) since 1992. He holds B.Tech. and Ph.D. degrees in chemical engineering from the Indian Institute of Technology, Kanpur, and the University of Delaware, respectively. Before coming to WVU, he taught at the State University of New York at Buffalo for 11 years. He has also worked briefly for the Monsanto and DuPont Companies, and he serves as technical advisor to the Polymers Alliance Zone of West Virginia. His research focuses on polymer rheology, polymer processing, and polymer composites. He is the author of *Polymer and Composite Rheology* and the co-author of *Fundamentals of Polymer Engineering.*

Elliot B. Kennel holds an M.S. degree in nuclear engineering from The Ohio State University and a B.S. in physics from Miami University (Ohio). He is a co-founder of Nanographite Materials, Inc., and Pyrograf Products, Inc. While working for the U.S. Air Force Research Laboratory in the early 1980s, he helped sponsor some of the early work in the creation of p-type doped carbon nanotubes and nanocomposites as a means of achieving high-temperature electrical conductors. Currently, Kennel is developing coal-based feedstocks for low-cost nanomaterials and other carbon products such as pitches and cokes.

Previously, Kennel served as vice president and director of research and development at Applied Sciences, Inc. (Cedarville, Ohio), and prior to that he served in the U.S. Air Force Research Laboratory as an officer and then civil servant in the area of aerospace materials and energy conversion.



Kwang-Jea Kim is currently at the University of Akron as a research faculty member. He obtained a Ph.D. degree in polymer engineering from the University of Akron after receiving an M.S. degree in surfactant synthesis at Inha University in South Korea where he continued his research work as a postdoctoral fellow. He worked for Struktol Company of America as a research scientist and project manager for more than five years and later at the chemical engineering department of West Virginia University as a research assistant professor for one year. His research focuses on polymer composites, interfacial science, rheology, reactive processing, chemical additives, nanomaterials, organic and inorganic hybrid materials, and rubbers and plastics. He is the co-author of *Thermoplastic and Rubber Compounds: Technology and Physical Chemistry*. He is currently serving as a guest editor of *Interfaces of Cellulose Polymer Composites*, which specializes in the wood–plastic composite area, and represents special issues of *Composite Interfaces*.

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Contents

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Overview of Challenges and Opportunities

Rakesh K. Gupta, Elliot B. Kennel, and Kwang-Jea Kim

CONTENTS

1.1 Introduction to the Book

Nanomaterials, and, in particular, nanoreinforcements for polymer composites have in recent years been the subject of intense research, development, and commercialization. A remarkable 1959 talk by Nobel Laureate Richard Feynman at the meeting of the American Physical Society at Caltech is recognized by many scientific historians as a salient event in the history of nanotechnology.[1] In his talk, Feynman foresaw the development of nanomaterials, nanolithography, nanoscale digital storage, molecular electronics, and nanomanufacturing methods. Among other things, Feynman famously offered two prizes, for a thousand dollars apiece, in which he asked for a working motor smaller than 1/64 of a cubic inch; or to anyone who could reduce text to the size such that only an electron microscope could read it (i.e., nanolithography). Both prizes were awarded within a few years.

Nanomaterials are an important subset of nanotechnology. Feynman was interested not only in the small dimensions that might be created, but also in the special attributes of materials whose size might be controlled to only a few atomic layers in thickness. These attributes, taken together, help to more precisely define the concept of nanomaterials. That is, nanomaterials of interest should not only have very small physical dimensions, but should also exhibit some unusual properties by virtue of their small size; and moreover, the producers of these materials should have control over the dimensions of the materials and hence the resultant property enhancements.

On this basis, it might be argued that a tire made of rubber compounded with carbon black was one of the earliest primitive nanocomposites. As early as the 1860s, the ability of carbon black to enhance the mechanical properties of vulcanized rubber was recognized by researchers who experimented with adding different materials to the basic rubber formulation. By virtue of its high surface area, surface energy, and mechanical properties, carbon black is able to significantly enhance the properties of rubber. Other well-known nanoscale reinforcements available in the early twentieth century included fumed silica and precipitated calcium carbonate.

Today, industrial applications of nanomaterials can be found in a wide variety of industries. Most readers would be familiar with applications in the field of electronics and in health care. These, however, are not all. Synthetic textiles incorporating nanopowders that endow the fabrics with antibacterial, flame retardant, non-wetting, or self-cleaning properties are becoming common. Thick coatings composed of nanoparticulate metal oxides find use in waterfast ink-jet media with photo-parity, while thin coatings can be used for optical amplifying systems for light-emitting diodes. Thermal spray of nanopowders allows for the coating of flight- and land-based turbines where corrosion or erosion must be prevented. Other applications may be found in buildings and construction, in automotive and aerospace components, and in environmental remediation and energy storage technologies. In the United States, the National Nanotechnology Initiative that was begun about a decade ago has aided these efforts.

As the name suggests, polymer nanocomposites are polymer-matrix composites but contain materials having at least one dimension below about 100 nm, wherein the small size offers some level of controllable performance that is different from the expectations developed in the macroworld. The notion is that there must be some advantage in achieving the nanoscale whether it is for mechanical reinforcement or for the enhancement of another desirable property. If the nanocomposite (e.g., a polypropylene carbon nanotube composite) were to have identical properties to its macroscopic counterpart (e.g., the same polypropylene reinforced with chopped carbon fiber derived from a polyacrylonitrile precursor), then there would be little point in developing nanocomposites in the first place. The challenge, then, is to create structures either by whittling down large features or by engineering atoms such that materials and devices have novel mechanical, chemical, electrical, magnetic, or optical properties.

The first nanoclay composite, in which silicates were used as a means of influencing the macroscopic properties of the composite, was described in a patent from the National Lead Company in 1950, which describes the use of clays to reinforce elastomers.[2] Yet, very little commercial activity proceeded from this patent, and it would be nearly four decades later before Toyota (Okada et al.) would patent a nanoclay-polyamide system in 1988, which was probably the first time that the molecular layering of silicates was recognized to be a key in transferring nano-properties to the macrocomposite.[3] Thus, this was a true polymer nanocomposite and can be regarded as a key milestone in the modern nanocomposite era. Following this development, Toyota launched the first commercial automotive application of polymer nanoclay composites, with a Nylon-6 timing belt cover in 1993.[4–6] By 2001, Toyota was producing body panels and bumpers containing nanoclays. Similarly, General Motors began using nanoclay composites for step assists on its GM Safari and Chevrolet Astro models in 2002.

Special mention should be made of carbon-based nanomaterials. Prior to 1980, it was thought that only two allotropes of carbon existed: (1) the diamond lattice and (2) the graphite lattice. A single plane of densely packed sp2-bonded carbon atoms arranged in a hexagonal close-packed configuration is referred to as graphene. Graphite, then, consists of multiple layers of graphene. However, by 1996 when the Nobel Prize in Chemistry was awarded to Robert F. Curl Jr., Sir Harold W. Kroto, and Richard E. Smalley, it was clear that at least a third allotrope existed—the so-called "buckyball" or C-60 atom. The nickname derives from the similarity between C-60 of the geodesic dome structures designed by the architect Buckminster Fuller. This can be considered a watershed event in the history of nanomaterials, as it catalyzed a flurry of research on nanotechnology in various fields, not only materials science. Later, other carbon molecules were discovered, such as C-72, C-76, C-84, and even as high as C-100.[7] Later, as a thought experiment at least, it was suggested that single-walled carbon nanotubes (SWNTs or SWCNTs) might be considered as very large elongated fullerenes.[8] A SWCNT consists of a single graphene layer wrapped into a tubular shape. In practice, however, these nanomaterials are grown with the aid of a metal catalyst particle, and thus the identification of nanofilaments with fullerene molecules is mainly a theoretical one.

Multiwalled carbon nanotubes (MWNTs or MWCNTs) consist of several layers of graphene wrapped into tubular shapes. Carbon nanofibers (CNFs) are considered to consist of layers of truncated conic sections or "stacked cups" of graphene.[9] Some variants of such nanomaterials had semiconductor characteristics, whereas others were electrically and thermally conductive, similar to metals. Potentially, these materials could have an enormous range of applications, including nanoelectronic devices, pharmaceuticals, and catalyst supports. Putting aside for the moment the practical objections of cost (about a million dollars per pound in the early days, except that no one could produce as much as a pound), the reported mechanical properties led materials scientists to wonder if practical composites could be made with nanoreinforcements. Individual nanotubes were said to offer strength, modulus, and strain values many times greater than those of steel.

Thus, from the standpoint of compounding polymer nanocomposites, filamentary carbons seemingly offer the prospect of significantly influencing mechanical properties. Initial attempts at fabricating polymer nanocomposites, however, did not result in the expected level of performance. Indeed, the nanocomposite properties were often inferior to the neat polymer, causing materials scientists to revisit their textbooks and to study the problems such as the material interface at the nanoscale as well as agglomeration and dispersion of nanoscale additives. In particular, polymer matrix materials must bond to the graphene surface of nanotube fillers. However, the surface energy of nanotubes is usually very low (e.g., analogous to Teflon®). Functionalizing the surface may provide a means to improve bonding to nanotubes, although the functional groups would presumably damage the graphene lattice. Consequently, the mechanical properties of carbon nanocomposites have not necessarily proven exceptional as of the first decade of the twenty-first century. Yet other properties may be just as important.

Electrically and thermally conductive polymer composites can be of interest for many niche applications. For example, even their weak electrical conductivity can render polymers suitable for electrostatic paint spraying, resulting in a less-expensive and an environmentally attractive process due to less wasted paint and elimination of the need for a primer coat. Alternatives such as chopped microfiber composites are not always viable due to the effect of the fibers on surface finish. Surface finish is often very important for automotive applications, obviously. Hyperion Catalysis, Inc., was one of the first producers of multiwalled nanotubes (MWNT) to bring nanocomposites to commercial status, based on the electrostatic paint spray application, as Ford Motor Company introduced MWNT nanocomposites in mirror housings on the 1998 Ford Taurus.[10] Thus, like their nanoclay cousins, carbon nanotube composites found early commercial success in the automotive industry, at a time when many scholarly researchers were unaware that these materials had been reduced to commercial practice. This may be partly due to the innocuous trade name (Fibrils™) used by Hyperion to market its material.

1.2 Organization of the Book

This book is divided into five main sections:

Section 1: Overview
Section 2: Nanomaterials and Surface Treatment
Section 3: Processing
Section 4: Structure Characterization
Section 5: Properties

1.2.1 Section 1: Overview

Chapters 1 and 2 are of an introductory nature. Chapter 2 reviews the history of carbon nanofilaments of different types from Gary Tibbetts, who at General Motors Research was an early pioneer in nanosynthesis, with the intention of producing low-cost commercial reinforcements for the automotive industry.

1.2.2 Section 2: Nanomaterials and Surface Treatment

Chapters 3 through 5 are concerned with surface treatment. In Chapter 3, Henry Ashton of Schneller Corporation provides an introduction to the incorporation of nanomaterials of different types into polymer media. In the case of the hydrophilic nanoclays, one needs to coat the clay surface with alkylammonium or other organic cations that are compatible with hydrophobic polymers. The coatings, however, can be thermally unstable and can decompose at the processing temperatures of some polymers. Solving this problem remains a challenge for the future. Chapter 4, authored by Kwang-Jea Kim and James L. White of the University of Akron, discusses the key issues of nanoparticle dispersion and reinforcement, including the effect of surface modification and additives such as chemical coupling of silanes on silica surfaces and its effect on the reduction of silica agglomerate size. Coupling conditions such as temperature, moisture level in the silica, and conditions affecting the particle dispersion are also introduced. Chapter 5 is particularly devoted to the modification of carbon nanoreinforcement surfaces to promote bonding with polymer matrix materials, and it is written by Max Lake and Jerry Glasgow, two pioneers in the development of carbon polymer nanocomposites.

1.2.3 Section 3: Processing

Chapters 6 through 11 deal with issues of processing nano-additives into polymer melts. Although the right chemistry is very helpful in facilitating the dispersion of nanofillers into polymers, extruders and other mixers must necessarily be used for the manufacture of polymer nanocomposites. The practical issues of compounding of layered silicate nanocomposites with thermoplastics using a twin-screw extruder are introduced by Paul Anderson of Coperion in Chapter 6. In Chapter 7, authored by Kwang-Jea Kim and James L. White of the University of Akron, a parallel treatment is provided to the processing of various nano-sized particles into elastomers using various processing instruments with various processing conditions. Chapter 8, on nanocomposite rheology and written by Subhendu Bhattacharya, Rahul Gupta, and Sati Bhattacharya of RMIT University in Australia, reviews what is known about the flow behavior, especially the dynamic mechanical behavior of different polymer and filler combinations. This information is needed for the successful conduct of subsequent shaping operations.

Chapter 9 introduces the fundamentals of polymer carbon nanocomposites, written by Enrique Barrera of Rice University. Barrera was one of the first persons to investigate the use of true nanotubes in polymer composites. Chapter 10, by Tatsuhiro Takahashi and Koichiro Yonetake of Ymagata University, recognizes the importance of controlling the physical alignment of nanotubes, and thus provides specialized insight into the use of electromagnetic fields to align carbon nanotubes within polymer nanocomposites.

Chapter 11, authored by Chang H. Song and Avraam I. Isayev of the Institute of Polymer Engineering at the University of Akron, explores the formation of nanofibrillar structured liquid crystal polymer (LCP) dispersed in polyester matrices during processing of unidirectional sheets and fibers. Polyester blends and operating conditions were examined to determine the main factors affecting the tensile strength and Young's modulus.

1.2.4 Section 4: Structure Characterization

Although a variety of techniques are employed to characterize the structure of polymer nanocomposites, x-ray diffraction and transmission electron microscopy (TEM) are the most common ones encountered. TEM, in particular, is the only method that actually allows one to see the microstructure. It is, however, a very tedious and labor-intensive technique. Vin Berry of West Virginia University explains the fundamentals of electron microscopy and its different variations in Chapter 12.

1.2.5 Section 5: Properties

Chapters 13 through 18 are devoted to the specialized properties attained from both clay-based and carbon-based nanocomposites. First, Chapter 13, authored by Leszek Utracki of the National Research Council of Canada, discusses the mechanical properties obtained from nanoclay polymer composites. Note that nanocomposites having the theoretical strength and stiffness of ideal, defect-free nanocomposites are now a reality.[11] Chapter 14, by Daniel De Kee and Kyle Frederic of Tulane University, describes mass transport issues through polymer nanocomposites. Controlling mass transport is one of the main drivers for considering nanoclay additives.

Similarly, flammability reduction is another objective with great commercial importance. Properties related to flammability and their potential enhancement with nanoclay additives are discussed in Chapter 15 by Charles Wilkie of Marquette University and Jin Zhu of YTC America, Inc.

Chapter 16, written by Elliot Kennel of West Virginia University, discusses the enhanced electrical properties of carbon nanocomposites. Chapter 17, which discusses the enhancement of thermal conductivity using nanoadditives, was written by Sushant Agarwal and Rakesh Gupta of West Virginia University.

Chapter 18 discusses specific niche nanocomposites. This chapter, by Chang-Kook Hong of Chonnam National University in Korea, and by Jue Lu and Richard P. Wool of the University of Delaware, delves into bio-nanocomposites from plant oil.