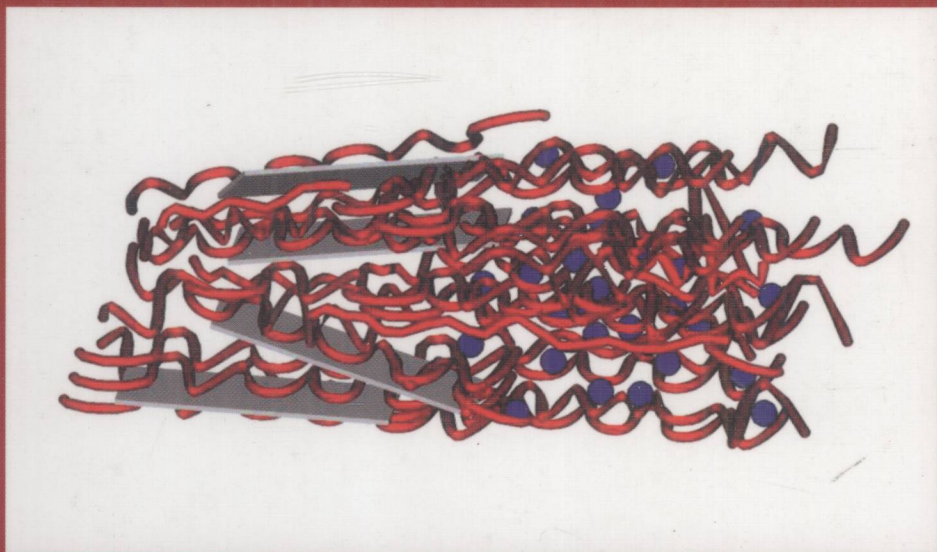


POLYMER—LAYERED SILICATE and SILICA NANOCOMPOSITES



Y.C. KE AND P. STROEVE

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Polymer-Layered Silicate and Silica Nanocomposites

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Polymer-Layered Silicate and Silica Nanocomposites

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Preface

Nanotechnology can be dated back to the 1860s when the field of colloid science was first established and when the colloid size range was defined from 1 to 1000 nm. Colloid scientists have studied materials in the nm range since that time. Over 80 years ago, life scientists, interested in the internal properties and functions of cells, began to look at structures at the nanoscale inside the cell. In the 1980s, the synthesis and investigation of new materials with size scales below a fraction of a micron became popular in many other fields. Some scientists predicted that, on the nanoscale, the properties of materials are quite different from those on the bulk scale. The preparation and study of nanoparticles became an active area of research. The use of nanoparticles in materials has become a central issue. The main problem in the application of nanoparticles is how to disperse the superfine particles into a matrix. When reviewing the technologies related to the dispersion of nanoparticles, it can be observed that the previous technology used for the dispersion of μm -sized particles is often employed. Many works deal with the surface treatment and interfacial design of nanoparticles, but the effective dispersion of nanoscale powders is still a major problem. Nanoscale particles with extremely high surface area and energy have a strong tendency to cluster. Agglomerated nanoparticles still account for a large part of nanoparticles dispersed in a matrix.

To deal with the dispersion problem, we took an opposite approach. We used a layered compound as an intermediate or precursor to prepare nanoscale materials through a step-by-step process, in which the μm particles are exfoliated into particles of a smaller size. In our approach, the larger particles become smaller and smaller, forming nanoscale particles, which is opposite to the agglomeration process in which the smaller nanoparticles become larger and larger. Fortunately, when naturally nanostructured layered silicates are used as the precursor, their interlayer distance can be pillared larger by the intercalation of foreign molecules or cations into the gallery space through an ion exchange reaction, and the silicate can be completely exfoliated by in situ polymerization.

Since 1994, research on polymer-layered silicate nanocomposites was started in China with support from the Natural Science Foundation of China (NSFC). The research was led by Prof. Z.N. Qi and F.S. Wang and, due to their and related scientists' efforts, nanotechnology and science on organic-inorganic nanocomposite became an emerging field in China. At the same time, several similar materials were developed by A. Usuki at Toyota, T. J. Pinnavaia at Michigan State University and P. Giannelis at Cornell University. Today, advanced research on organic-inorganic nanocomposites is conducted in different parts of the world.

Polymer-layered silicate and silica nanocomposites are important in China because of their applications to engineering, electronics, plastics and petrochemical fields. With

financial support from the Ministry of Science and Technology (MOST), the China Academy of Sciences (CAS), the Natural Science Foundation of China (NSFC) and corporations such as BASF (Germany), Sinopec (China) and CNPC (China), we have prepared and studied many advanced materials. Since 1996, we have applied for more than 20 patents in China for a series of nanocomposite materials, including polyesters (PBT, PET), polyolefins (PP, PE), polyamide and PI with layered silicates and silica. These materials have been used to make functional films, plastic bottles, coatings and engineering plastics. Some of these applications are summarized in our final reports to the financial organizations supporting the research, in postdoctoral reports, doctoral dissertations and the book *Polymer-Inorganic Nanocomposites* published in Chinese by China Chemical Industry Press.

When developing a series of polymer-layered silicate and silica nanocomposites, we made a breakthrough in fabricating plastic barrier bottles. Inspired by the success of silica nanoparticle preparations at a large scale developed by L.D. Zhang at the China Academy of Sciences (CAS), we prepared several nanocomposite materials with assembled, or array patterns, of monodisperse silica nanoparticles. Additional nanocomposite materials with arrays of silica were prepared with our collaborators. Composites with silica particles as small as 20 nm were also prepared.

We first attempt to present the nanocomposite materials with advanced properties, explore nanoeffects and develop the dispersion technology. As is shown above, our research obtained strong financial backing from MOST, NSFC and the national corporations. Meanwhile, at the University of California, Davis, layer-by-layer film technology was being studied in order to create nanoparticle/ultrathin film structures. We decided to join forces and combine our research efforts. We made a book proposal to Elsevier for publishing our research and partial related works from our collaborators.

This research monograph deals with nanocomposite materials of organic polymer-layered silicate, organic polymer-silica and layer-by-layer polyion nanoparticles. It focuses on the nanomaterial's classifications, preparations, characterization, applications and material properties. It also reports on our development of nanotechnology and processing of the polymer-layered silicate and silica nanocomposites.

The authors
Changping, Beijing, China
August 21, 2004

Acknowledgements

This research monograph reviews our research and the research of colleagues with whom we have collaborated. In addition, review the work of researchers who have had a significant impact on our own work. Thus, this book is a reflection of the research of many individuals and groups in the area of nanocomposites and nanoparticles. A number of years ago, Prof. Z.N. Qi and Prof. F.S. Wang conducted their ground-breaking research on polymer– inorganic nanocomposites in China and they wrote a book – *Preparations and Theory of Polymer-Layered Silicates Nanocomposites*, which was published by China Chemical Industry. Their work has had a tremendous impact on our research. Further, they have given us helpful advice and memorable guidance.

Most of the work in this research monograph comes from the final reports of several projects, which were supported by the Ministry of Science and Technology (MOST), the China Academy of Sciences (CAS), the Natural Science Foundations of China (NSFC), and the companies BASF (Germany), PetroChina, CNPC (China) and Sinopec (China). Some pictures and graphs in the book are from postdoctoral reports written by Prof. Y. C. Ke, the senior author of this book.

Some researchers and professors provided original material and gave us permission to publish their work in our book. We thank our colleagues Prof. Q. Li, Prof. L.D. Zhang, Prof. P. Dong, Prof. J.N. Yan, Prof. Y. Cai Ke, Dr. Z.J. Xue, Y.M. Ma and others for providing us with such information. We appreciate their kindness.

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CHAPTER 1

Background on Polymer-Layered Silicate and Silica Nanocomposites

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In this chapter we introduce general concepts, the methods of preparation of nanoparticles and nanocomposites and classifications of different technologies, e.g., intercalation chemistry and sol-gel processes. Classical colloidal theory and its applications to nanocomposites are also discussed.

Introduction

In polymer-layered silicate and silica nanocomposites, the polymers used are those that are universal. Layered silicate are those minerals that assemble regularly with the unit crystalline layer, usually at the nanoscale. Minerals are montmorillonite (MMT), kaolinite, sepiolite, etc. In this book, the word clay is a general name for layered silicate minerals, and specifically refers to MMT if not otherwise pointed out. Silica in this book refers to multiple dispersed silicon oxides, monodispersed silica particles and its powders.

The book mainly deals with the preparation of polymer-layered silicate and silica nanocomposites, their structure-property relationships and the related nanoeffects. Some key aspects are specifically emphasized, such as the in situ preparation of solid precursors for nanoparticles and nanocomposites, the proper dispersion of nanoparticles in selected inorganic or organic matrixes, particle surface treatment and in situ polymerization. With the development of ultrafine particles and their applications, the dispersion techniques for micrometer particles are introduced for nanoparticles to obtain ideal homogeneous morphology [1]. From the previous literature, the dispersions of both nanoparticles and micrometer particles are mentioned in several sections of this book. Our primary goals are to show how to enhance the organic polymer properties by making nanocomposite materials of polymers and silicate. We think of nanocomposites as materials to improve the properties of traditional organic polymers. Improved properties of polymer materials are of great importance in applications in the petrochemical industry, the chemical industry, materials and allied fields.

In this book, layered silicates are designed by in situ dispersion into polymer matrixes through a method called "intercalation," in which polymer monomers are intercalated into the gallery space of layered silicates, causing the layers to exfoliate before polymerization reactions are initiated. Finally, the polymer-layered silicate nanocomposites are discussed. Most layered silicates themselves have strong dispersion and cation exchange properties in many media, e.g., water and ethanol, which is why silicate are selected as raw materials for fabricating nanocomposites. Layered silicate contains certain quantities of non-metals, such as silicon, proteins, iron oxides and titanium elements. These materials can be harmful and lead to unstable or not useful crystalline structures. Thus, silicate should be purified and transformed into "polymer grade clay" [2]. To a large extent, intercalation polymerization based on layered silicates creates a way to prepare and disperse nanoparticles in organic polymer matrixes. Preparation techniques are designed to avoid nanoparticle agglomeration during dispersion. However, dispersed particles tend to form

aggregates during dispersion. Particles piled together without separation or particles forming interconnected agglomerations have to be avoided in order to enhance the material properties of the nanocomposite. Thus, researchers have sought ways to avoid the agglomeration of particles. At present, *in-situ dispersion* is an established technology for dispersing fine particles in materials. In this book, we show how layered silicates are fabricated by in situ dispersion in a polymer matrix by a method called *intercalation*, in which polymer monomers are intercalated into the spacing of layered silicates, after which the layers are exfoliated once the polymerization reaction is initiated. In this manner, nanocomposites of polymer silicates can be prepared.

According to our previous works [3–5], a layered silicate as a candidate for preparing a nanocomposite must meet requirements based on its structural unit, stable ingredients, reactive properties, high-performance–cost ratio and available resources in nature. We give more details below.

Structural units. The most important reason for layered silicates to be a candidate in preparing nanocomposites is their unit layer structure. The unit structure scale is 1 nm or so, and usually forms a nanophase in situ in a polymer matrix during its compounding or polymerization. There is also a requirement that the layers be expandable and easily exfoliated during formation of the nanocomposite. Generally, the layer interdistance must be expandable in solvents such as water and alcohol.

Stable ingredients. Most layered silicates have no stable ingredients, but they have ambiguous features such as unknown compositions, variable elements or transitional elements such as Fe, Ti and their oxides.

Reactive properties. Reactive properties refer to the layered structure taking part in different reactions including copolymerization reaction with the surface hydroxyl groups, catalytic reaction, etc. Specifically, the layered silicate should not pose an obstacle to polymerization during the exfoliation process.

High performance–cost ratio, and readily available resources in nature. The selected mineral as a candidate in preparing nanocomposites on an industrial scale requires that the cost is appropriate based on the performance of the nanocomposite. This depends on a good performance to cost ratio.

In this book, a great number of nanocomposites of polymer silica are introduced and discussed. This will naturally lead to questions about the suitability of silica for nanocomposites. Similar to the layered silicates with surface hydroxyl groups, ultrafine silica is also suitable for in situ polymerization through proper surface treatment. This silica is generally prepared in a form called “core–shell” structures, where the silica is in the core position, while polymer or oligomer film is outside of the particles. The core–shell particles have their scale usually greater than pristine silica but they exfoliate during further compounding, or during in situ polymerization with polymer monomers.

1.1. Layered silicate

1.1.1. Nanostructures in nature

Nanostructures in nature can be found in various forms. Naturally formed nanostructures exist not only in non-living forms but in living forms as well. In biological systems, there

exist a great variety of complex self-assembled nanostructures in organelles, cells, tissues and organs. Nature tends to arrange itself into nanostructures. Nature's ordered structures and patterns are very useful for study. Organic macromolecules and biological molecules have been designed by nature to build nanostructures or composite structures in biological systems [5]. Molecular self-assembly is of great interest to scientists and has stimulated research in nanotechnology and nanoscience.

In this book, nanostructures in nature refers specifically to those found in minerals, and specifically to layered silicates. In different minerals, such as MMT, illite, talc, saponite, attapulgite and mica, layered structures of nanometer size can be found. The natural nanostructures in layered silicates are also seen in man-made materials such as the carriers ZSM-5, MCM-42, MCM-41 and zeolite [6], which are used in the petrochemical industry. These materials have either nanometer-size pores or nanoscale particle structures. The carrier materials are prepared by copying natural nanostructures such as the zeolites, which have pore diameters from several nanometers to several tens of nanometers. When catalysts such as P_d , P_t and R_h are dispersed as nanoclusters on the surfaces of the carrier materials, the resulting catalytic materials are used for oil cracking. In particular, when Ziegler–Natta catalysts are deposited on the carrier $MgCl_2$ [5], or its mixture with silica, the active catalyst components are from 1 nm to several tens of nanometers thick and are suitable for polyolefin polymerization.

Extensive work in the literature indicates whether the minerals are of natural occurrence or man-made, and is the natural nanostructures can be identified. The International Union of Pure and Application Conference (IUPAC) [7] has given a definition for the pore diameter of these materials (see Table 1.1). According to this definition, porous carriers are called nanoporous and are different from nanoparticles themselves. Materials with either nanopores or nanoparticles are generally defined as nanomaterials.

1.1.1.1. Some milestones in nanoscale science and technology

In 1959, the Nobel Prize Physicist Richard Feynman asked “what would happen if we could arrange the atoms one by one the way we want them?” in one of his question lectures at the University of California. His question is thought to be the theoretical origin of the creation of modern nanotechnology and nanoscience. The development of the atomic force microscope (AFM) and the scanning tunneling microscope (STM) by IBM in the 1980s was another milestone [8,9]. The invention of scanning nanoprobe microscopies has stimulated the development of nanotechnology and nanoscience in the last 20 years.

In 1989, the Argonne National Laboratory (USA) facilitated the establishment of a company based on nanophase materials and also organized a meeting on nanometer

Table 1.1
IUPAC classification for pores

Pore classification	Pore diameter (nm)
Micro-pore	< 2
Medium pore	20–50
Large pore	> 50

science and technology. In 1992, the first scientific magazine on nanomaterials, *Nanostructured Materials*, appeared. In the 1980s and 1990s, the synthesis of carbon nanotubes and C_{60} Buckey Balls stimulated the interest in nanotechnology and nanoscience. Around 1997, several companies were created that produced nanomaterials (e.g., Nanophase Technologies and Nanocor).

In the 1980s, scientists in China suggested that new alloys with new metal crystalline phases could be made using metal superfine powders below micrometer scale [11]. Research in this area was published in a book on nanomaterial science [12]. These events are thought to be the beginning of nanomaterials and their applications in China. Work on nanomaterials and nanotechnology in China has been discussed in several recent books, [5,10].

On the other hand, one can easily find discussions of many chemical methods for preparing nanoparticles, nanopowders and nanoscale materials in the literature of the past century. For example, the sol-gel technique is well known for preparing different forms of nanomaterials. Historically speaking, colloid chemistry has been known for more than a century, and in this field one can find procedures for the preparation of many nanomaterials. Colloid chemistry defines colloidal particles as particles that range in from 1×10^{-9} to 1×10^{-6} m (or 1–1000 nm), which is partly in the nanoscale. This proves that concepts such as nanosize, nanoscale and nanoscience have, an effect, been known for more than a hundred years.

1.1.1.2. Formation of concepts for nanomaterials and nanotechnology

While it might seem to be too early to, give a complete definition of nanomaterials and nanotechnology, we have to present such concepts in our teaching, lectures and books for engineering students. Together with other related literature, this book will use the following expressions to describe nanoscience and nanotechnology.

- (1) Nanometer: a unit for nanomaterials, often abbreviated as nm.
- (2) Nanoscale: a scale within nanometers.
- (3) Nanoparticle: a nanoscale particle.
- (4) Nanostructure: a nanoscale structure, usually a structure revealed under scanning probe microscopy, e.g. TEM and AFM.
- (5) Nanomaterial: a material in which many nanoparticles with nanoscale structures are dispersed or aggregated.
- (6) Superfine or ultrafine powder: refers to powder materials with their particles at the nanometer scale.
- (7) Nanotechnology: The U.S. National Nanotechnology Initiative (NNI, 2000) and other sources describe nanotechnology as a technology for synthesizing nanomaterials by controlling single atom behavior at the molecular level and creating new molecular structures. Nanotechnology deals with matter showing novel and markedly improved character when the structure and composition of the matter system within 1–100 nm. Nanotechnology falls aims at the development of information on nanostructures, the invention of analytical equipment to investigate the characteristics of nanostructures based on groups of atoms, molecules and supramolecules, and the creation of processes to produce nanostructures for useful applications.

1.1.1.3. Nanocomposites

1.1.1.3.1. Definition of composites In polymer science, the word composite is well known. In brief, composites are generally two or more closely interacting materials in intimate contact with each other. Intimate contact can be down to the atomic or molecular level. Polymer science uses the concept of a composite as a material formed by combining different phases. There are many ways of combining phases and these are: filling, blending, compounding, mixing, melting and assembling. These terms are well known in scientific papers dealing with composites, especially those related to material or polymer science. Though a composite is not easily defined or briefly described, this book will adopt the definition of the concept of a composite as it is used in polymer science.

1.1.1.3.2. Composite materials According to the International Organization for Standardization, composite materials are solid ones with multiple phases, which is a combination of two or more materials with different physical and chemical properties [12]. In composite materials, one phase is usually continuous and called the matrix, while the other phase is a reinforcing material called the dispersed phase. In self-assembled systems, the ordered structure is the dispersed phase, while the template film can be the continuous phase.

Organic–inorganic composite materials. This refers to composite materials in which one phase is made up of organic molecules or polymers and the other of inorganic molecules or polymers. Thus, polymer–inorganic composites belong to this category.

Organic–inorganic nanocomposites. In organic–inorganic composites, nanocomposites refer to composites in which the inorganic phase has nanoscale morphology such as particles, fibers and tubes. There is an additional type of organic–inorganic nanocomposite, where either the organic phase or the inorganic phase has nanoscale morphology in an organic–inorganic composite [5,12]. For example, in emulsion systems of W/O or O/W, clay nanoparticles and silica are often used to stabilize the emulsions, which then form an organic–inorganic nanocomposite. In designing a system of thiol/FeOOH, heating the mixture would lead to the formation of thiol/Fe₂O₃ or thiol/Fe₃O₄ nanocomposites [5].

Polymer–Inorganic nanocomposites. Generally, it refers to a nanocomposite in which organic polymer forms a composite with inorganic nanoparticles, e.g., BiI₃–nylon nanocomposite [13], and montmorillonite–nylon (polyester) nanocomposites [7].

1.1.1.4. The classification of nanocomposites

This book gives our classifications of nanocomposites based on a review of the literature.

- (1) **Classification 1.** This classification is based on the nanomaterial's dimensional (D) morphology.
 - (a) 0-D nanopowder or nanoparticle;
 - (b) 1-D nanowire, nanowisp, nanosilk, nanotube or nanocrystalline whisker;
 - (c) 2-D nanomaterial with morphology of layer, lamellar or belt structure;
 - (d) 3-D nanomaterial with morphology of cylinder, solid or block structure.
- (2) **Classification 2.** This classification is based on polymer morphology, shape or state in the nanocomposites, in which the inorganic particle is a 0-D nanoparticle [5,14].

- (a) 1-D nanocomposite when the polymer in the composite is in solution;
 - (b) 2-D nanocomposite when the polymer in the composite is in film or membrane shape;
 - (c) 3-D nanocomposite when the polymer in the composite is in a powder state or morphology;
 - (d) 0-D nanocomposite formed with two different nanopowders.
- (3) *Classification 3*. This classification is based on a nanophase of tube- or non-tube-like material in the nanocomposites.
- (a) *Tube-like*, e.g., single-wall carbon nanotube, TiO_2 Tube, or Al_2O_3 tube.
 - (b) *Non-tube-like*, e.g., layer of clay, lamellar, silk, belt or band-like shape.

Sometimes, the classifications are mixed to describe nanocomposites, e.g., carbon nanotubes or nanocrystalline whiskers with polymer powder construct a 1–3 type nanocomposite. Nanolayers of clay with polymer powder form 2–3 type of nanocomposites, etc. The classifications for nanomaterials or nanocomposites are of definite significance with respect to the so-called “nanoeffect,” which is related to the material properties of the composite (mechanical, optical, thermal and magnetic) and the dependence of the properties on the size of the nanoparticles in the nanocomposite.

1.1.1.5. *Nanoeffect*

Besides the particle’s shape, surface or morphology, dispersion and aggregation in a matrix, attention needs to be paid to the properties and performance of a composite. How nanoparticles affect the properties of nanocomposite materials is of concern to engineers and scientists who are interested in the applications of nanocomposites.

1.1.1.5.1. Critical scale The nanomaterials or nanocomposites and the theories related to them are based on a concept of “critical scale,” or nanoscale. For a critical scale of nanoparticles, the nanocomposite properties produce a superior property compared with the pure counterpart matrix if the nanoparticles are below a critical size. When a material structure has one dimension less than the critical scale of 100 nm, can appear totally different the behavior of its material properties. Based on such phenomena, scientists determined the abnormal phenomena to be produced on the scale level between single-atom molecules and clusters of many thousands of molecules. Properties of any nanocomposite must include two aspects: “nanoscale” and “nanoeffect.” At a critical scale, the properties of nanocomposite materials can sometimes produce an inverse transition of a property, e.g., the conduction behavior of the metal Ag will change into that of an insulator at a particle scale less than 14 nm, while ferric magnetic performance is transformed into supermagnetic if the cluster size becomes less than several nanometers.

1.1.1.5.2. Nanoeffect in nanocomposites Nanoeffects in nanocomposites have several forms such as acceleration of polymer crystallization, induction of crystallization in a polymer, induction of liquid crystalline phenomenon, abnormal optical phenomenon, e.g., a blue shift, and abnormal multiple melting behavior, e.g., double-melting behavior in PET-layered clay nanocomposites. In addition, several forms of nanoeffects related to optical–electrical transition, electrical–magnetic transition and system properties are introduced in the book.