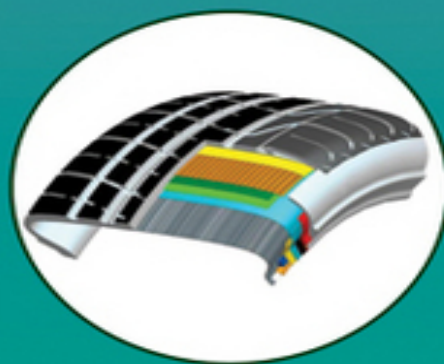
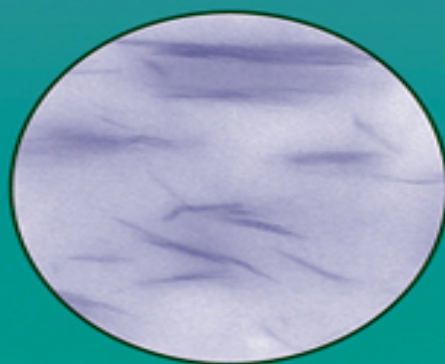
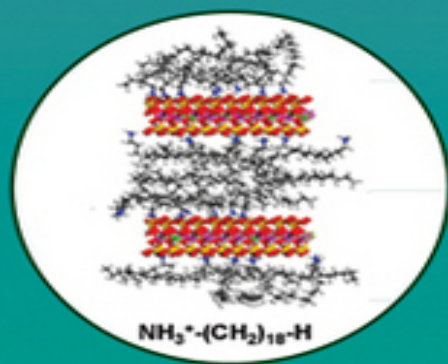


RUBBER-CLAY NANOCOMPOSITES

Science, Technology, and Applications



Edited by
MAURIZIO GALIMBERTI

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Preface

A New Generation of Fillers for Rubbers: *Nano-Fillers*

The properties of rubbers have always fascinated the human mind. “I wonder why the night, as a rubber, is of endless elasticity and softness” wrote a novelist [1] and the inventor of vulcanization, Charles Goodyear, reported “There is probably no other inert substance the properties of which excite in the human mind an equal amount of curiosity, surprise, and admiration. Who can examine and reflect upon this property of gum-elastic without adoring the wisdom of the Creator?” [2]. Rubbers are indeed fundamental materials for the human life but their properties are not sufficient for their applications, not even after vulcanization. To achieve the required physical-mechanical properties, rubbers have to be reinforced with the so-called reinforcing fillers.

The addition of carbon black was observed to improve the physical properties of vulcanized rubbers already at the beginning of twentieth century, although its use was delayed by consumers resistance to the black color. The first synthetic rubber tires in a car, of Emperor Wilhelm, were of a white color. Fillers such as carbon black and silica were developed all over the last century and allowed to improve a large set of rubber properties, such as impermeability, tear, fatigue and abrasion resistance, while simultaneously increasing antagonistic properties such as modulus and elongation at break: this phenomenon is known as the paradox of elastomers. Carbon black and silica are made of spherical primary particles, with an average size in a range from 5 to 100 nm, and are present in the rubber matrix as aggregates that cannot be separated via thermomechanical

mixing, having dimensions up to several hundreds of nanometers.

Over the past two decades, new characters appeared on the scene of fillers for polymeric materials, the so-called *nano*-fillers: they can be dispersed in a polymer matrix as individual particles with at least one dimension at the nanoscale. This nanometric size is correlated with features such as a huge specific surface area, a very low concentration for establishing a network in a polymer matrix (what is known as the percolation threshold) and also, often, a high length-to-width ratio, that is, a high aspect ratio. Most researches performed both in the academic and industrial fields on polymer composites with *nano*-fillers, that is, on polymer *nano*-composites aimed to exploit the enormous potential of *nano*-fillers.

Clays As *Nano*-Fillers for Rubbers

Among *nano*-fillers, clays undoubtedly play a major role. These layered silicates are available as inexpensive natural minerals and, as in the case of the most diffused cationic clay, montmorillonite, are considered to have a safe toxicologic profile, as they appear to have little chance to cross biological barriers. They are thus suitable for large scale applications and were used to prepare novel rubber/inorganic materials. Clays are hydrophilic and need to be compatibilized with the hydrocarbon rubber matrix: the most applied organophilic modifiers, ammonium cations bearing long-chain alkenyl substituents, are able to build up a variety of crystalline arrangements in the interlayer space. The so-formed organically modified clays promote a multiscale organization in the rubber matrix, from its distribution and dispersion to a reorganization of the organic

moiety between two opposite layers, potentially involving the polymer chains. The onium modifiers are also known as efficient accelerators of the cross-linking reactions. Moreover, all these aspects depend, to a different extent, on the type of rubber adopted as the matrix. All these aspects are degrees of freedom but represent at the same time a complexity for the development of these novel rubber materials.

Rubber-clay nanocomposites (RCN) have been extensively investigated. Hundreds of papers are available in the scientific literature, with a large number of data and some proposed interpretations. Some industrial applications have already been successfully brought to a commercial scale, backed by hundreds of patent applications and based in particular on the improvement of mechanical properties as well as of impermeability. However, in spite of the large scientific investigation and of some commercial applications, the potential of clays in imparting new properties to a rubber composite could be exploited to a much larger extent.

Why A Book on Rubber-Clay *Nano-Composites*?

This book moves from the awareness of the state of the art of RCN and its identity is determined by the following objectives. To make available an updated recollection of data, interpretations and theories reported in the open scientific literature. Time is mature for proposing a rationalization of what so far discovered, to the benefit of both students and professionals. A further objective is to allow scientists and technologists working in the field to critically review the common perception of RCN, building a sound cultural base, prodrome of further R&D activities and

further innovations. As a key feature of this book, items involved in RCN science, technology, and applications are discussed providing a comprehensive overview from clay structural features to application (e.g., in an automotive part). This book wishes thus to contribute to a better exploitation of RCN potential.

A Brief Summary of the Book

This book is organized in four sections.

In the first section, clays and organoclays for rubber composites are introduced. In Chapter 1, Bergaya et al. present natural and synthetic clay minerals, from crystallographic structure to fundamental aspects such as the multiscale clay organization and, in particular, the intimate organization of the layers. Most relevant clay physicochemical properties are also discussed. Clay modification with the preparation of organoclays is covered by the same authors in Chapter 2, analyzing the fine-tuning of organoclays properties. The industrial treatments of a bentonite clay is discussed by Della Porta in Chapter 3: processing, purification, reaction with organic substances. Heinz illustrates in Chapter 4, the alkylammonium chains on layered clay mineral surfaces: structure and dynamics, thermal and mechanical properties, layer separation, and miscibility with polymers. Giannini et al. deal with chemistry of rubber-organoclay nanocomposites in Chapter 5, from their thermal decomposition to the interaction with the sulfur-based vulcanization chemistry.

The second section is dedicated to preparation and characterization of RCN. Zhang et al. present in Chapter 6 the processing methods for the preparation of RCN, in particular latex and melt compounding, from mechanism to influencing factors. Galimberti et al. rationalize the RCN morphology in Chapter 7: the multiscale organization in the

rubber matrix is discussed for pristine clays and organoclays, as a function of processing method, type of rubber, and in particular of the organic modifier. Mechanisms proposed for the formation of intercalated and exfoliated clays are critically reviewed. Isaev et al. deal with RCN rheology in Chapter 8, taking into consideration various types of rubbers and providing an overview of proposed theories. Vulcanization characteristics and curing kinetic of RCN are discussed by Lopez Manchado et al. in Chapter 9, focusing the attention on the role of organoclay in a vulcanization reaction and on the influence of its structural characteristics. The mechanical and fracture mechanics properties of RCN are reviewed by Reincke et al. in Chapter 10, dealing with viscoelastic and mechanical properties, fracture behavior and mechanisms, theories and modeling of reinforcement. The permeability of RCN is covered by Rodgers et al. in Chapter 11, with particular reference to butyl type rubbers, to influencing factors such as rubber vulcanization and temperature and to an important application such as the one in a tire compound.

The third section is dedicated to RCN based on a particular type of rubber. Karger-Kocsis et al. deal with apolar diene rubber and with nitrile rubber in Chapters 12 and 13, respectively. RCN based on butyl and halobutyl rubbers are covered by Magill et al. in Chapter 14. Makoto and Koo et al. discuss RCN based on olefinic rubbers and thermoplastic elastomers in Chapters 15 and 16, respectively. Preparation methods are covered, key aspects such as barrier, vulcanization, mechanical properties are discussed.

In the final section, main applications of RCN are presented. Bandyopadhyay et al. discuss automotive applications in Chapter 17 and Feeney et al. present in Chapter 18 nonautomotive applications such as the one for sport balls.

Last but not the least, as the editor I wish to acknowledge the work of all the authors, done with much involvement and enthusiasm. We felt as a team, with the common aim to give a profitable contribution to all the readers.

I would like finally to acknowledge the work done by my coworkers, Valeria Cipolletti and Michele Coombs, in editing this book.

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Section I

Clays for Nanocomposites

Chapter 1

Clays and Clay Minerals

Faïza Bergaya

Maguy Jaber

Jean-François Lambert

1.1 What's in a Name

The term “clay” was used in everyday language long before being imbued with a well-defined scientific meaning. Therefore, it is not surprising that it carries different connotations to different communities. To the industrialist, it is a raw *material* available in large amounts at cheap prices, characterized by its macroscopic properties relative to various applications. To the geologist working in the field, it is a particular secondary *mineral* largely found in weathered deposits from sedimentary or volcanic origin. To the chemist and mineralogist, it refers to a particular type of mineral *structure* defined at the atomic level.

Recent recommendations of the JNC¹ advise to use the term “clay minerals” to refer to precisely determined crystallographic structures, and define “clays” in terms of macroscopic properties.² Therefore, a natural clay will consist of a/several clay minerals mixed with additional minerals as impurities. However, the distinction is not always clearly made and many papers that use well-defined

clay minerals will refer to them as “clays” because the full denomination is somewhat cumbersome [1].

Here we will build on the crystallographic view, which is the most rigorous, and try to indicate how the atomic structure dictates the properties at other levels.

The most salient structural feature of clay minerals is that they are layered. That is to say they belong to a large class of inorganic compounds built by the stacking of two-dimensional units, known as layers, whose internal coherence is due to strong iono-covalent bonds, while in the direction perpendicular to the stacking they are bound to each other through weaker forces. This means that the layers can be separated from each other relatively easily, and the volume included between two successive layers, whatever its content, is called the “interlayer space” (the term “gallery” or “intergallery space” was formerly used synonymously but has to be discarded). A macroscopic analogy would be a pile of paper sheets, or may be a deck of cards depending on the semirigidity assumed for the layers.

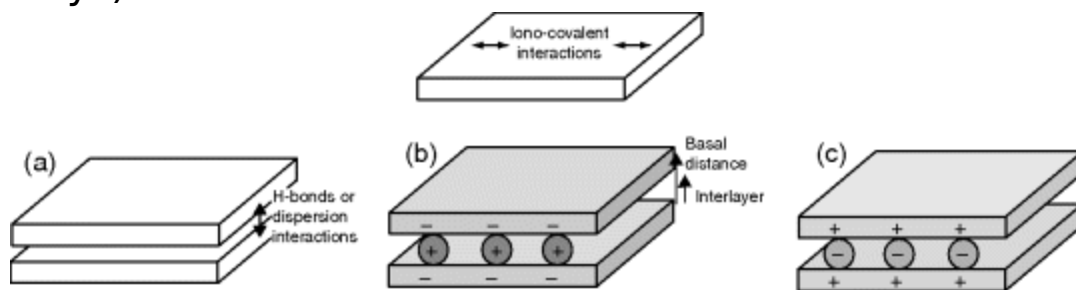
Clay minerals are a subset of the family of layered oxides (or oxyhydroxides), which can be classified in three different categories according to the electrical charge of the layer ([Figure 1.1](#)):

- i. Neutral layers, as in pyrophyllite, talc, and kaolinite. The layers are held together by van der Waals interactions and/or hydrogen bonds.
- ii. Negatively charged layers. Since the structure as a whole must be neutral, the negative layer charge must be compensated exactly by an equal amount of positive charges provided by cations located in the interlayer space (compensating cations). These minerals are most often listed as phyllosilicates, and the most widespread in nature (especially montmorillonite which is the major component of commercial bentonites) belong to this

group, and are therefore called “cationic clays” when specification is needed.

iii. Positively charged layers with compensating anions in the interlayer space. The most common natural mineral in this group is hydrotalcite (HT), but this belongs to a broader family of “HT-like” materials most often synthesized in the laboratory and called layered double hydroxides or LDH. These are also called “anionic clays” [2–4].

Figure 1.1 The basic architecture of a clay mineral at the nanometric scale: (a) neutral layers; (b) negatively charged layers with compensating cations (cationic clays); and (c) positively charged layers with compensating anions (anionic clays).



It should be noted that we have characterized clay minerals as layered “oxides” or “oxyhydroxides” rather than layered silicates (or “phyllosilicates”). Indeed some of them do not contain any silicon in their formula (the LDH) and thus are certainly not silicates. Even in the case of cationic clays, an argument could be made that the term “silicate” obscures the real structure of the layers (as outlined in Section 1.3.1.3 and corresponding inset) and is a leftover from a time when only the raw formula was known.

Let us come now to the clay as a macroscopic material. Historically, the criterion of particle size has been used a lot to define clays, although different disciplines and professions have fixed different size limits. The “clay fraction” has been defined as fine-grained materials with a

maximum particle size (or, rather, an equivalent spherical diameter) $\leq 2 \mu\text{m}$.

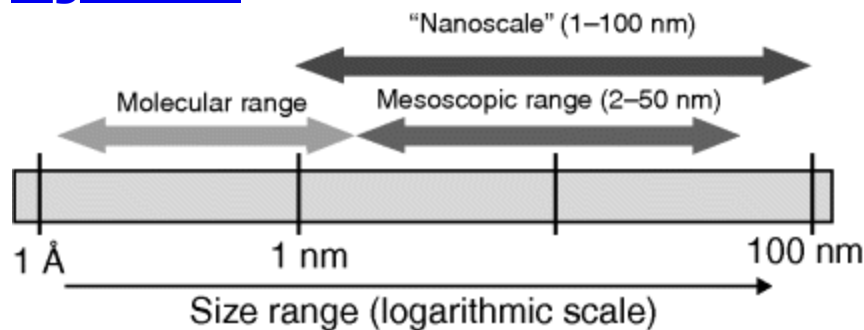
However, the particle size limit used by different communities could vary from $1 \mu\text{m}$ (for colloid scientists) up to $4 \mu\text{m}$ (for engineers; see Ref. [5]. It is not considered as good practice any more to set a well-defined size limit to clay minerals [1], although the particles must be small enough to form colloidal dispersions in water. More than a definition, the size criterion is a practical recipe for separation since particles with different sizes will sediment at different rates in water, according to Stokes's law [6] (which states that the settling velocity of a particle in a fluid is proportional to the square of the particle radius, all other things being equal) — the finest clay fraction can thus be obtained by centrifugation at the laboratory scale, even though industrialists use other methods to separate large quantities of clays for practical reasons (see Chapter 3).

Materials commercially available as clays may be (i) raw clays, containing several other associated minerals (carbonates, cristobalite, feldspars, quartz, etc.) and other associated X-ray amorphous phases (organic matter, iron hydroxides, etc.) as contaminants in addition to clay minerals proper or (ii) clay mineral fractions obtained by sedimentation, fragmentation, and/or several other treatments aimed, for example, at eliminating iron oxide impurities by selective dissolution. The recommended procedures to obtain pure clay mineral samples are reported in more details by Carrado et al. [7]. For some applications, *de novo* synthesis of clay minerals may be more attractive compared to the complexity of purification processes of the raw clays. Synthetic cationic clay minerals may indeed be prepared with high purity (cf. Section 1.5), but their cost will of course be higher than that of natural clays.

The JNC has kept among the clay-defining criteria some referring to specific properties that are relevant to their

application as materials: plasticity in the presence of water, hardening on drying. In these properties, the behavior of clays in the presence of water plays an important role. We will therefore consider the behavior of clays in the presence of aqueous phases, first at a nanoscopic level, which includes mesoscopic level as shown in [Figure 1.2](#), and later at a molecular level.

Figure 1.2 Mesoscale, nanoscale, and molecular scale.



1.2 Multiscale Organization of Clay Minerals

Clay minerals form pastes, then gels, when the amount of water is increased or other polar solvents are added to the dry solid, and that translates a specific organization of the dispersed solids in the presence of the solvent.

That organization is largely similar to the one that exists in native clays; in the simplest scheme, three successive levels of organization can be defined at different scales: in descending order of size, aggregates, particles, and layers [1, 8].

1.2.1 Dispersion Versus Aggregation

At the upper level (macroscopic), the sample is made of millimetric-size aggregates. Upon closer inspection, the aggregates are seen to consist of a number of flat micrometer size particles (sometimes called *platelets*; the