

## Synthesis and Structure of Intercalated Organo-inorganic Nanocomposites

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The synthesis and structure of organo-inorganic nanocomposites prepared by intercalation of monomers or polymers into the interlayer galleries of layered matrices are analyzed. General features and the mechanism of the intercalation process, as well as materials used for this purpose, mostly often naturally occurring materials (clays, silicates, layered phosphates, chalcogenides, and other moieties hosts), are discussed.

Mechanisms governing the intercalation of monomers or polymer repeating units into the interlayer galleries as guests are compared. One of the most widespread and commercially important intracrystalline chemical reactions is the incorporation of monomer molecules into pores or layered lattices of the host substances with subsequent post-intercalation transformations into polymer, oligomer, or hybrid-sandwich products. Particular emphasis is placed on nanocomposites based on epoxy polymers and various mineral matrices. Basic application areas of hybrid nanomaterials are considered.

**Keywords:** Nanocomposites, Intercalation, Epoxy resins, Metal nanoparticles, Hybrid nanomaterials, Clays, Polymerization.

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### 1. INTRODUCTION

A nanocomposite is the product of coupling of at least two dissimilar substances having a distinct interface, even if one of them should have at least one dimension in the nanometer size range (1–100 nm).

This circumstance also refers to distances between networks and layers formed by polymer and inorganic components [1,2]. In other words, a polymer nanocomposite is a two-phase material in which organic and inorganic phases are distributed in each other at the nanolevel. Materials in which monomer or polymer molecules are intercalated (embedded) as guests into the structures of hosts, most often of natural and more rarely of synthetic origin, belong to precisely this class. Rigid crystalline matrices of the host with a controlled system of percolation pores with nanometer sizes can also be filled by atomic or molecular structures of the guests: nanoparticles of metals; their oxides; inorganic coordination polymers; and large molecules, such as dyes and fullerenes [3, 4]. In kinetic terms, such a topotactic process is characterized by a low activation energy of diffusion and the materials thus prepared are usually metastable and cannot be synthesized by other methods (e.g., by the thermal synthesis) because of delamination-exfoliation of components.

### 2. GENERAL FEATURES OF THE INTERCALATION PROCESS

The intercalation properties of these materials are determined by characteristics of their internal open-porous systems—pore sizes. In terms of architecture and properties of pores, intercalation systems are divided into two types. The first type is characterized by rigid pores with constant volume, parallel isolation of lattice channels, and communicating channels of the host network. Localization, concentration, and spatial

distribution of guests are defined by the topology, chemical nature, and reactivity of the internal surface of the host whose matrix may be additionally functionalized. The types of guests are limited by the smallest crosslinked channels. This ensures their selective intercalation behavior in matrices (just as in molecular sieves). The second type of guests is presented by the low-sized lattice of the host, that is, the layered or chain structure. This provides flexible pores whose sizes may adapt to the sizes of the guest. In layered systems, the basal (intralayered) space formed by sandwich OH groups of octahedral aluminum hydroxide or oxygen atoms of tetrahedral silicate sheets achieves about 5  $\mu\text{m}$  and the thickness of the layer (e.g., in perovskite) varies from 0.5 to 2.2 nm.

In the general case (for dispersion of clay particles in polymer matrices), the following types of intercalated nanocomposites may occur: a phase-separated microcomposite; intercalated nanocomposite, and delaminated (exfoliated) nanocomposite.

Traditional phase-separated microcomposites, which are prepared by mixing of components, among them those in polymer melts, include clay tactoids with layers aggregated in the unintercalated form. An inorganic component is simply dispersed as a separate microphase in the polymer matrix, and the system thus formed represents a monolithic microscale structure. Delaminated or exfoliated nanocomposites are made up of layers of host delaminated nanoparticles (or delaminated suspensions) with a thickness of the order of 1 nm. The degree of layer separation depends on the polymer content in a composite and governs its properties.

In this case, MMT lamellas act on polymer chains as nanosized hosts and affect the structure and orientation of macromolecules, especially when the system is crystallized from the melt. Probably, the most interesting intercalation compounds with a definite structure are formed upon intercalation of one or more polymer

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molecular layers into the host clay gallery. In these nanocomposites, interaction between components is the strongest since the surface of layers of organic and inorganic components is maximally accessible to interactions. As a rule, this leads to a significant improvement of mechanical properties.

### 3. POLYMERIZATION IN THE INTRALAYER SPACE

The most intriguing type of intracrystalline chemical reactions is the incorporation of monomer molecules into the host pores and subsequent controlled transformation into polymeric, oligomeric, or hybrid sandwich products (intercalation transformations, in situ processes). This method is frequently referred to as an in situ ship-in-the-bottle polymerization of preintercalated monomers or this approach is called polymerization filling.

Specifically, polymer aluminosilicate nanocomposites containing a few percent of an intercalated or exfoliated polymer manifest improved properties as compared to the unfilled polymer: mechanical strength, thermal stability, and incombustibility along with good barrier behavior and chemical resistance.

Lamellar aluminosilicates are often used as hosts in the polymerization of acrylic monomers. The type of nanocomposites thus prepared is affected by the concentration and nature of a monomer as well as the synthesis conditions and procedure. Monomer molecules intercalated via the precursor displacement approach form new hydrogen bonds; as a result, various types of guest based compounds arise. For example, kaolin-methanol intercalation compounds are employed as intermediates in substitution reactions involving relatively large guest molecules: *n*-nitroaniline,  $\Sigma$ -caprolactam, alkylamines, vinylpyrrolidone, etc.

The intercalation polymerization holds great potential for design of organo-inorganic nanocomposites in the course of their formation. Chain propagation that proceeds under strong steric hindrances and growing internal stresses in the interlayer space may be accompanied by the formation of polymers differing in both structure and behavior from those in the case of free-chain propagation. This situation affects the properties of the final products.

### 4. DIRECT INSERTION OF MACROMOLECULES INTO HOST LAYERED LATTICES

This strategy may be realized via various approaches: mixing of components, enveloping a polymer into a gel, the employment of polymer solutions or melts, etc.

Among the most typical cases are nylon-layered silicate nanocomposites, hybrid epoxide-clay nanomaterials, and nanomaterials based on hectorite and polyaniline (including those from acid-methanol solutions of poly(aniline hydrochloride), polythiophene, or polypyrrole). In the general case, hybrid structures of two types may form in these nanocomposites, namely, intercalated structures in which a polymer (or a part of its units) is incorporated between silicate layers and exfoliated (delaminated) structures, in which silicate layers are dispersed individually in the polymer matrix, while giving rise to a monolithic microscale structure. As in the polymerization variant, mostly layered silicates, Na-MMT, including those modified by long-chain amines, are employed. On the basis of melted polymers (PE, PP, PS, PEO, nylon, etc.), polymer-clay composites are prepared in which the clay is, as a rule, modified by various substrates beforehand [5, 6, 7]. Sometimes, various modifying additives are introduced into the polymer melt to improve its compatibility. Maleic anhydride (MA)—a well-known compatibilizer—is most frequently used for this purpose. Interphase agents change the rheology of melts, the interparticle structure, and the chemistry of hybrid materials. One typical case of direct polymer intercalation is the insertion of PEO into layers of flat silicates of the mica type. This process is achieved by the interaction of polymer melt with the Na<sup>+</sup> or exchange lattice of the host. For the intercalation of water-soluble polymers (PEO, PVP, polyethylenimine (PEI)), the encapsulation precipitation from solution is employed.

The intercalation of polymers into interlayer galleries of inorganic materials is an extensively and fruitfully developing area of polymer science. Intercalation chemistry provides practically unlimited opportunities for designing hybrid organo-inorganic nanocomposites. At present, basic phenomena accompanying formation of these materials have been revealed, their structural organization has been determined, and their potential features have been ascertained, especially for modern perspective applications.

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