

The advantages and disadvantages of clay nanofillers

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Abstract

Cílem této bakalářské práce bylo popsání výhod a nevýhod jílových nanoplňiv. Nejprve byla věnována pozornost různým typům jílových plniv a způsobům jejich přípravy, tudíž hlavní část této práce spočívá v charakterizaci jílu, jílových minerálů a pod ně patřících fylosilikátů. Jíly se dělí do 7 základních podskupin a z toho vyplývá, že každá z těchto skupin má určitou strukturu a také specifické využití. Jako nanoplňiva se nejčastěji používají minerály ze skupiny smektitů. Z tohoto důvodu je podstatná část práce zaměřena i na popsání dalších nanoplňiv jako jsou kaolinity a vermikulity. V závěru je obecný souhrn poznatků o výhodách a nevýhodách nanoplňiv.

The aim of this Bachelor thesis was depicting the advantages and disadvantages of clay nanofillers. Firstly, the attention was paid to the different types of clay fillers and the methods of their preparation. Therefore, the main part of this thesis is based on the characteristic of clay, clay minerals and phylosilicates, which are the main and the most important part of clay. Clays are divided into seven basic subgroups. So, each of them has specific both structure and utilization. Minerals from smectite group are used as nanofillers the most frequently. From this reason, the thesis is especially concentrated on the description of other nanofillers like kaolinites and vermiculites. In conclusion, there are the summary of the key advantages and disadvantages of nanofillers.

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INTRODUCTION

Nowadays, the attention of scientist is focused on creating revolutionary material combinations on nanoscale. So, nanotechnology is mainly concentrated on both making and utilization of the inorganic nanoparticles from carbon, clay, silicate, ceramics and other materials.

Polymer nanocomposites are a new class of emerging materials. Their originality compared with conventional composites consists in using filler with one of its dimension at least in the nanometer range. A clay mineral is a potential nanoscale additive because of its compression silicate layers in which the fundamental unit is 1 nm thick planar structure.

Almost all scientists occupy with research of montmorillonite, which is the most proved clay nanofiller. But lately attention of scientists turns in other nanofillers like kaolinite, which has the similar properties as montmorillonite and is a very cheap raw material of the tile industry. On the other hand, there are necessary steps including refining and chemical modification prior to the melt intercalation step.

By tailoring the clay structure in polymers on the nanometer scale, novel material properties have been found. Clay particles can provide large improvements in mechanical, thermal and gas-barrier properties without raising the density of the compound and reducing light transmission. So, these materials can have many potential applications, such as packing films.

Finally, there is necessary to understand the mechanism of the enhancement effect for the development of clay/polymer nanotechnology.

1 NANOCOMPOSITES AND NANOMATERIALS

Nanocomposites are a new class of composites, for which at least one dimension of the dispersed particles, is in the nanometer range [1]. Materials science and chemistry are often engaged in research on the nanometer scale, for example, the dimensions of crystal structures. The well-known nanometer-scale technologies developed within material science and chemistry in the past may not be reasonably regarded as nanotechnology. The real interest in nanotechnology is to create revolutionary properties and functions by tailoring materials and designing devices of the nanometer scale [1], [2].

Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Nanomaterials are not simply another step in miniaturization, but a different area entirely; the nanoworld lies midway between the scale of atomic and quantum phenomena, and the scale of bulk materials. Development of nanotechnology has been spurred by refinement of tools to see the nanoworld, such as more sophisticated electron microscopy and scanning tunnelling microscopy.

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous. It is possible to find them in extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging film, superabsorbents, components of armour, and parts of automobiles. Their extremely small feature size is of the same scale as the critical size for physical phenomena. The way a crack grows in a larger-scale. Bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. However fundamental electronic, magnetic, optical, chemical, and biological processes are also different at this level.

Particular nanocomposites based on polymeric materials are one small division of nanomaterials. There are several varieties of polymeric nanocomposites, but the most commercially advanced are those that involve dispersion of small amounts of nanoparticles in a polymer matrix. Those most humble of materials, clays, have been found to impart amazing properties. Addition of nanoparticles not only improves the mechanical properties, but also has been shown to improve thermal stability. Clay/polymer nanocomposites have been considered as matrix materials for fiber-based composites destined for aerospace components [3].

Clay minerals are a potential nanoscale additive because of its content of silicate layers in which the fundamental unit is a 1 nm thick planar structure. Also, it undergoes intercalation with various organic molecules such as toluene and aniline. The intercalation causes an increase in the distance between silicate layers, which is dependent on the molecular size of the organic molecule.[4]

1.1 Polymer/clay nanocomposites

Polymer/clay nanocomposites have their origin in the pioneering research conducted at Toyota Central Research Laboratories where these two divergent organic and mineral materials were successfully integrated. Fittingly, the first practical application of a nanocomposite was in the use of a nylon-montmorillonite clay nanocomposite as a timing belt cover on a Toyota Camry automobile [4].

Polymer/clay composites are divided into four general types:

- *conventional composite* - the clay acts as a convention filler,
- *intercalated nanocomposite* - consisting of a regular insertion of the polymer in between the clay layers,
- *exfoliated nanocomposite* - 1 nm-thick layers are dispersed in the matrix forming a monolithic structure on the microscale.
- *flocculated nanocomposite* - this is conceptually same as intercalated nanocomposites. However, silicate layers are some times flocculated due to hydroxylated edge-edge interaction of the silicate layers. [5],[6],[7].

You can see in the Fig. 1 three types of composites.



Fig.1 Polymer/clay nanocomposites [6]

In contrast to emulsion polymer nanostructures, or to conventional composites, polymer/clay nanocomposites are the important class of the emerging new

nanocomposites. These materials have demonstrated significantly enhanced properties in a number of areas, frequently delivering a superior balance of previously antagonistic properties.[6]

1.2 Synthesis of Polymer/clay nanocomposites

The preparative methods are divided into four main groups:

1.2.1 In- Situ polymerization

In-situ polymerization was the first method used to synthesize polymer-clay nanocomposites based on polyamide 6. This method involves inserting a polymer precursor (monomer in most cases) between clay layers and then their expanding and dispersion into the matrix by polymerization (see Fig. 2). Polymerization can be initiated either by heat or radiation, by the diffusion of suitable initiator or by an organic initiator or catalyst. The catalyst is fixed through cationic exchange inside the interlayer before the swelling of step by the monomer. This method is capable of producing well-exfoliated nanocomposites and has been applied to a wide range of polymer systems. The following polymers were prepared by this method: PA 6, PE, PET, PP and epoxy resin [6].

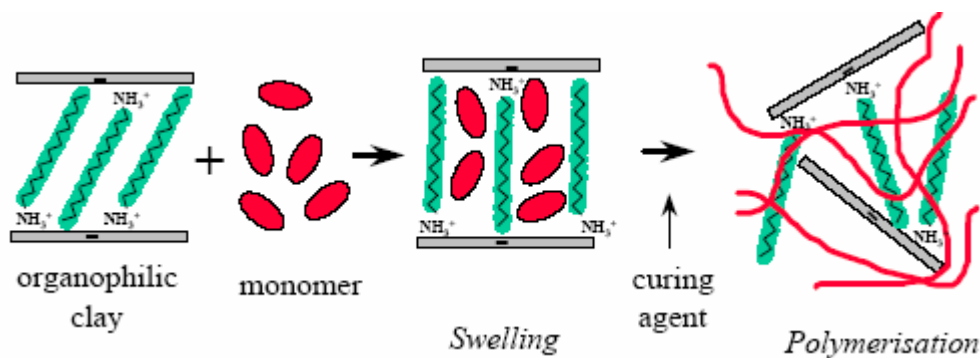


Fig. 2 The in-situ polymerization [5]

1.2.2 The solution-induced intercalation

The solution-induced intercalation method applies solvents to swell and disperse clays into a polymer solution. The layered silicate is exfoliated into single layers using a solvent in which the polymer is soluble. It is well known that layered silicates, owing the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets are reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer

structure. The major advantage of this method is that it offers the possibilities for the synthesis intercalated nanocomposites based on polymers with low or even no polarity. Water-soluble polymers, such as PEO, poly(vinyl acetate) (PVA), poly(2-vinyl pyridine) (PVP) and ethylene vinyl acetate copolymer (EVA), have been intercalated into the clay galleries using this method. Examples from non-aqueous solvents are nanocomposites of poly(ϵ -caprolactone) (PCL)/clay and poly(lactide) (PLA)/clay in chloroform as a co-solvent, and high-density polyethylene (HDPE) with mixture of xylene and benzonitrile [6].

1.2.3 Melt intercalation

In this method, the layered silicate is mixed with the polymer matrix in the molten state (see Fig. 3). Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. So, no solvent is required. The approach can be applied in the polymer processing industry in order to produce nanocomposites based on traditional polymer processing techniques, such as extrusion and injection moulding. The nanocomposites containing as a polymer matrix PE, PP, poly(etherimide), PS, SAN were prepared by this method [6]

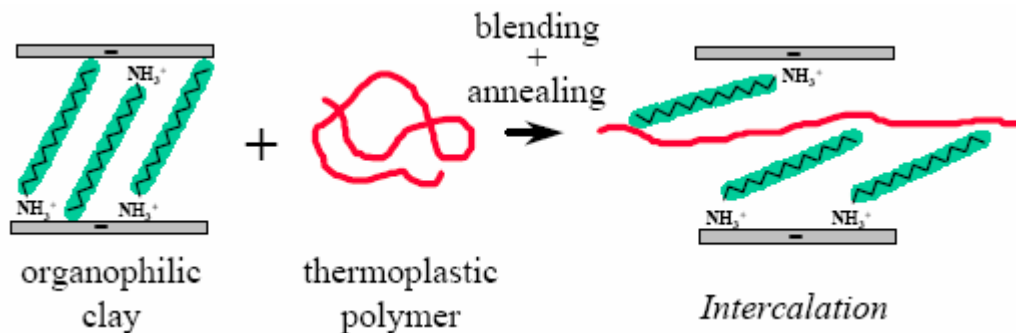


Fig. 3 The melt intercalation process [5]

1.2.4 Template synthesis

This technique, in which the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks, has been widely used for the synthesis of double-layer hydroxide-based nanocomposites. Unfortunately, it is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the

nucleation growth of the inorganic host crystals and is got trapped within the growing layers [1],[2],[5],[6].

1.2.5 The advantages and disadvantages of method synthesizing polymer/clay nanocomposites

The melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation. This method is the most common because neither a suitable monomer nor a compatible polymer-silicate solvent system is always obtainable. In addition to these major processing methods, other fabrication techniques have been also developed, for example, solid intercalation, vulcanization, and the sol-gel method. Some of these methods are in the early stages of development and have not yet been widely applied.

2 CHARACTERIZATION OF MATERIALS

2.1 Clay, organoclay and clay minerals

Common clays are naturally occurring minerals and are thus subject to natural variability in their constitution. The purity of the clay can affect the final nanocomposite properties [9].

The term **clay** is denoted by a particle size range and by certain physical properties. The particle size and properties can vary, depending upon the discipline that is operationally using the term. In geology, the term clay includes all particles that are $<2\ \mu\text{m}$. This size limited for clay is sometimes reported in $<4\ \mu\text{m}$ (such as in engineering). When the term "clay sized" particles is used, there are no connotations about composition. The term clay sized can constitute any material as long as it's within the particle size range is $<2\ \mu\text{m}$. Clay is often described as a fine grain material, that is plastic if it is wet and is chiefly composed chiefly of hydrous alumino-silicate minerals [8].

Clays are composed of two basic building blocks (see Fig.4):

- 1) Silicon - Oxygen Tetrahedron (SiO_4^{-4})
- 2) Aluminum Octahedral (Gibbsite Sheet) (AlO_6^{-9})

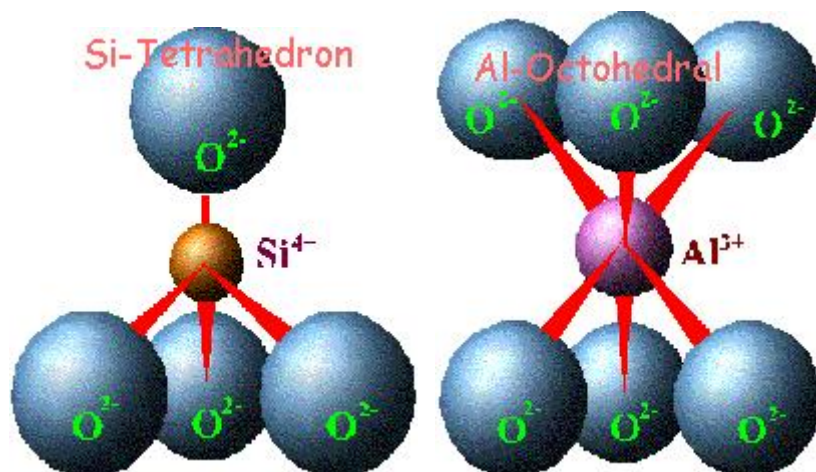


Fig. 4 Si-Tetrahedron and Al-Octahedral [21]

Tetrahedral sheets (see Fig. 5) are composed of individual tetrahedrons and three of four oxygens are shared in each of them (in summary $\text{Si}_2\text{O}_5^{2-}$). They are arranged in a hexagonal pattern with the basal oxygens linked and the apical oxygens pointing up/down.

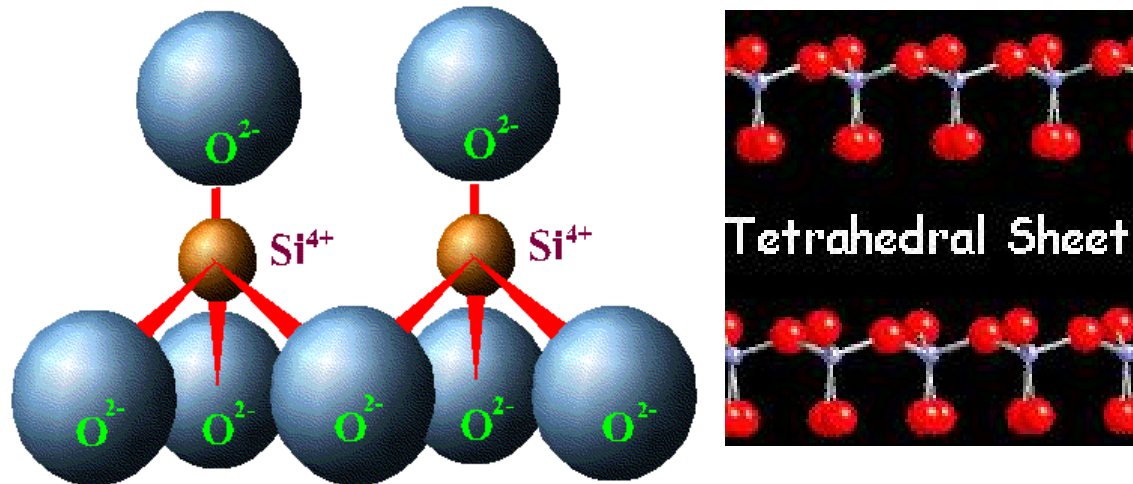


Fig. 5 The tetrahedral sheet [12],[21]

Octahedral sheets (see Fig. 6) are composed of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al^{3+} , Mg^{2+} , Fe^{3+} and Fe^{2+} typically serving as the coordinating cation. These octahedrons are arranged in a hexagonal pattern are known as gibbsite sheet [9], [10], [21].

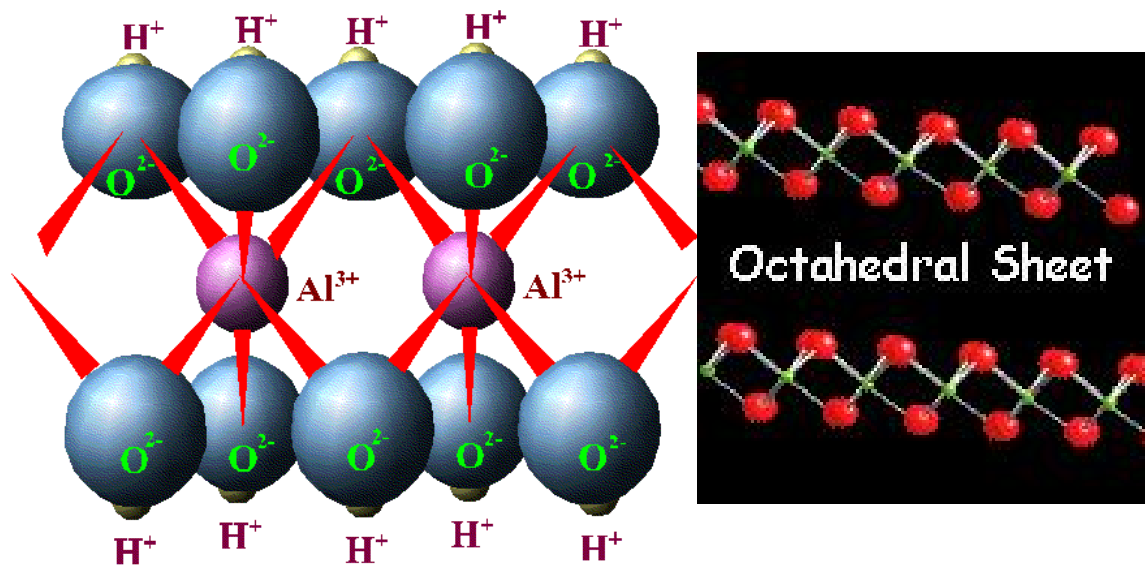


Fig. 6 The octahedral sheet [12],[21]

Most polymers are hydrophobic and are not compatible with hydrophilic clays. In this case, pre-treatment of either the clays or the polymers is necessary. The most popular methods for clay modification are the use of amino acids, organic ammonium salts, or tetra

organic phosphonium salts to convert the clay surface from hydrophilic to organophilic. The clays modified in this way are known as **organoclays** [2].

The clay minerals (according to website of Mineral Gallery) are the part of general but important group within the phyllosilicates that contain large percentages of water trapped between the silicate sheets. Most of clay minerals are chemically and structurally analogous to other phyllosilicates but contain varying amounts of water and allow more substitution of their cations [11]. On the other, hand author Weiss defines **the clay minerals** as groups containing all phyllosilicates and other minerals (such as minerals of allophane group, some hydroxide, oxy-hydroxide and oxides), that afford plasticity to clays and they can be cure after exsiccation or burning. These other minerals are only minority components of clays in contrast to phyllosilicates [14]. On the website of Mineralogical society of America **clay minerals** belong to the family of phyllosilicates and contain continuous two-dimensional tetrahedral sheets of composition T_2O_5 ($T = Si, Al, Be, \dots$) with tetrahedra linked by sharing three comers of each, and with the fourth corner pointing in any direction. The tetrahedral sheets are linked in the unit structure to octahedral sheets, or to groups of coordinated cations, or individual cations [30].

Phyllosilicates

The phyllosilicates, or sheet silicates, are an important group of minerals, where tetrahedron $[TO_4]$ and octahedron $[MA_6]$ are of interest for building the phyllosilicates. The central cations of tetrahedron are designated like T, and except the most frequent Si^{4+} they can include for example Al^{3+} , Fe^{3+} and Ge^{4+} . The central cations of octahedron are designated like M, and they can include for example Al^{3+} , Fe^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ca^{2+} and Li^{+} . The name A is used here for the reason that there are some anions of octahedron like O^{2-} but also OH^{-1} or F^{-1} in phyllosilicates [14].

The basic structure of the phyllosilicates is based on interconnected six member rings of SiO_4^{-4} tetrahedra that extend outward in infinite sheets. Three of the 4 oxygens from each tetrahedras are shared with other tetrahedra. This leads to a basic structural unit of $Si_2O_5^{-2}$ [13].

Phylosilicates are divided into two groups:

- 1) **Planar phylosilicates** - their structures include the continual two-dimensional periodic site of tetrahedron and octahedron.

Two types of structural unite produced by connection of tetrahedral and octahedral sites can be seen in the case of planar phylosilicates:

1:1 layers – when octahedral and tetrahedral sheet has one common plane of oxygenic atoms. 1:1 layers are constructed of one octahedral and one tetrahedral layer.

2:1 layers – when octahedral and tetrahedral sheet has two common planes of oxygenic atoms. 2:1 layers are constructed of one octahedral and two tetrahedral layers with opposite polarity [14].

- 2) **Unplanar phylosilicates** - their structures contains the periodic dislocation of planar phylosilicate structure. Moreover, in this case the planar structures can be bent or cylindrically rolled and even have the spheroidal character.

Diocahedral and trioctahedral minerals

The oxygen ions in the octahedral layer are in a close packed structure. The octahedral layer consists of two planes of oxygen ions. Each oxygen ion, is bonded with two smaller aluminum ions located in the space created between the larger oxygen ions. Extra sites, as can be seen in Fig. 7, are created when the oxygen and aluminum ions come together. There is one empty site on average created for every two aluminum ions in the structure across the entire octahedral layer. This situation presents an alternate possibility for building the mineral. Two trivalent aluminum ions provide the total of six positive charges but it is same for three divalent ions. Thus, during the process of mineral formation the octahedral layer might be filled with divalent ions rather than the aluminum ions. Often either divalent iron or magnesium is the ions replacing the aluminum. If the octahedral layer contains divalent ions in all the possible sites, it is known as the trioctahedral mineral. If this layer contains trivalent ions in two of every three possible sites, it is known as the diocahedral mineral.

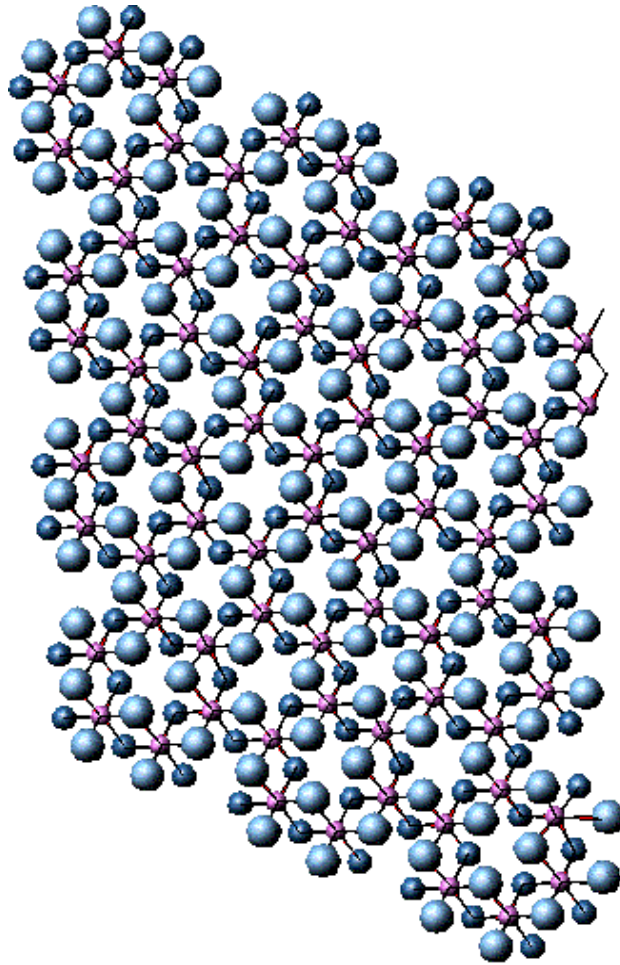


Fig. 7 Extra sites created when the oxygen and aluminum ions come together [12]

Clays are divided into 7 groups:

1. The Kaolinite group
2. The Montmorillonite/Smectite Group
3. The Illite (or The Clay-mica) Group
4. The Chlorite Group
5. Sepiolite and Palygorskite
6. Mixed-Layered Clays
7. Vermiculite [15]

2.1.1 The Kaolinite group

The primary structural unit of this group is the layer composed of one octahedral sheet and one tetrahedral sheet. In the dioctahedral minerals the octahedral sites are occupied by Fe^{3+} ions and one unit of tetrahedral sites by four O^{2-} and one Si^{4+} ions; on the other hand, in the trioctahedral minerals the octahedral sites are occupied by Mg^{2+} and Fe^{2+} ions and one unit of tetrahedral sites by four O^{2-} and one Si^{4+} ions.

Members of the kaolinite group include:

1. *The dioctahedral minerals:* Kaolinite, Dickite, Nacrite and Halloysite,
2. *The trioctahedral minerals:* Antigorite, Chamosite, Chrysotile and Cronstedite.

Kaolinite and halloysite have single-layer structures. Although dickite and nacrite have the same basic structure, but the stacking sequence of layers is different [16]. The vectors defining orientation of structural units of nacrite have slope of 60° and slope of dickite is in normal position. Antigorite is a rare sheet silicate found in many metamorphic and weathered igneous rocks. Its structure consists of flat layers of silica tetrahedrons bridged by molecules of brucite, $\text{Mg}(\text{OH})_2$ [28].

Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

It is known also as kaolin clay or simply kaolin. [20] Kaolinite is named because of its locality as Kao-Ling, Jianxi, China.

It is a 1:1 type layered clay mineral, which consists of SiO_4^{4-} tetrahedral sheets and $\text{Al}(\text{OH})_6^{-2}$ octahedral hydroxyl sheets. Neither cations nor anions are present in the interlayer space. Since the interlayer regions are surrounded by hydroxyl groups of the octahedral sheets on one side and the oxide arrangement of the silicate sheets on the other side, guest species are generally arranged with a specific orientation [15], [16]. The structure of kaolinite can be seen in the Fig. 8.

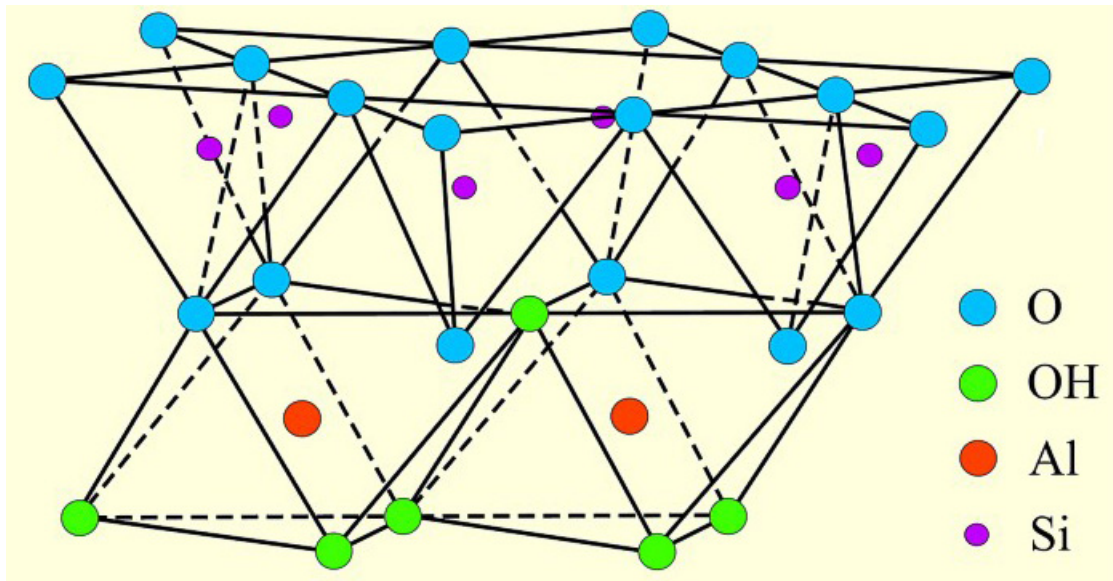


Fig. 8 The structure of Kaolinite [15]

The minerals of the kaolinite group do not swell in water: the polar water molecules find no reason to attach themselves to the neutral kaolinite structural unit. Not many ions are present in the interlayer sites, and therefore kaolinite is not a good cation exchange medium. Kaolinite is usually formed under low pH conditions, in acidic soils and hydrothermal spring regions, with abundant water present and intense chemical weathering [18].

The intercalation reactivity of kaolinite is low owing to its inherent hydrogen bonding between the layers. The intercalation of kaolinite has not been investigated as much as in the case of smectite group [4].

2.1.2 The Smectite group

The term smectite is used to describe a family of expansible 2:1 phyllosilicate minerals having permanent layer charge between 0.2 and 0.6 charges per half unit cell. Smectites are constructed of a single octahedral sheet sandwiched between two tetrahedral sheets. The octahedral sheet shares with the tetrahedral sheet the apical oxygens. The octahedral sheet may be either dioctahedral or trioctahedral [16]. The structure of this group can be seen in the Fig.9.

The most important aspect of the smectite group is the ability of H₂O molecules to be absorbed between the sheets. It can cause the increase of mineral volume when mineral

comes in contact with water. Thus, the smectites are expanding clays [13]. In other words, smectites swell in the presence of water, and also many organic liquids.

Members of the smectite group include:

1. *The dioctahedral smectites:* Montmorillonite, Beidellite, Nontronite and Volkonskoit.
2. *The trioctahedral smectites:* Hectorite, Saponite, Sauconite and Stevensit.

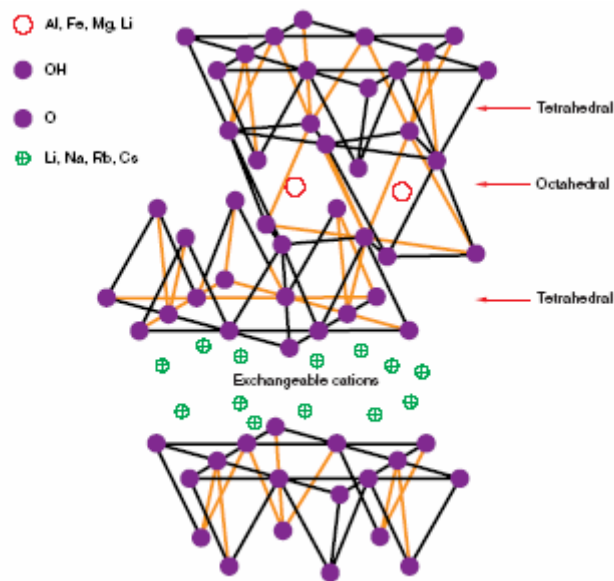


Fig. 9 The structure of 2:1 layered silicate [29]

The interlayer (the space between the sheets) is hydrated and expandable; that is, the separation between individual smectite sheets varies depending on:

- 1) The type of interlayer cations (monovalent cations like Na^+ cause more expansion than do divalent cations like Ca^{2+} ,
- 2) The concentration of ions in the surrounding solution,
- 3) The amount of water present in the soil.

The interlayer atoms are fairly loosely attached to the mineral surface, and therefore can be exchanged for other cations. For this reasons they are called **exchange cations**. For instance, if smectite clay with mainly Ca^{2+} ions comes in contact with sea water, they loose Ca^{2+} and accept Na^+ ions.

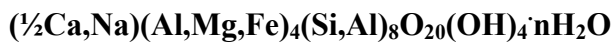
Cation exchange is a very important process in nature, and it partly regulates the natural water composition by absorbing and desorbing ions. The **cation exchange capacity (CEC)** is the measure of the charge imbalance of clay, and also the measure of the number of ions that can occupy the interlayer sites. The CEC varies according to the nature of the absorbed ions present in the interlayer sites. Kaolinite has very low CEC (3-15 meq/100g), whereas smectites may have large values (70-130 meq/100g) [18].

Soils having high concentrations of smectites can undergo as much as 30% volume change due to the wetting and drying. In other words, these soils have the high shrink/swell potential [21]. Unlike the other clays, only smectite can absorb toxins. This property qualifies its structural uniqueness and differentiates them from all other clays. For this reason, smectite has become favourite clay for industrial and dietary usage [19].

Montmorillonite

The most common dioctahedral smectite is Montmorillonite, discovered in 1847 in France (Montmorillon) by Damour and Salvétat. It is nowadays the most widely used clay as nanofiller.

The one of common formula of Montmorillonite (it depends on type of MMT):



The model structure (see Fig. 10) consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. The MMT layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns. MMT has a very high aspect ratio (e.g. 10–1000, one gram of this clay has a surface area of 800 square meters [19]). Isomorphous substitutions of Si^{4+} for Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet cause an excess of negative charges within the montmorillonite layers. These negative charges are counterbalanced by cations such as Ca^{2+} and Na^{+} situated between the layers. Due to the high hydrophilicity of the clay, water molecules are usually also present between the layers. Stacking of the layers leads to regular van der Waals gaps called interlayers or galleries.

There is the number of descriptive terms for MMT. It is mainly based on geographic source, exchangeable cations, production process, and end use application.

The most known MMT are the following:

Wyoming, Chambers, Otay and Fe-montmorillonite type [14]

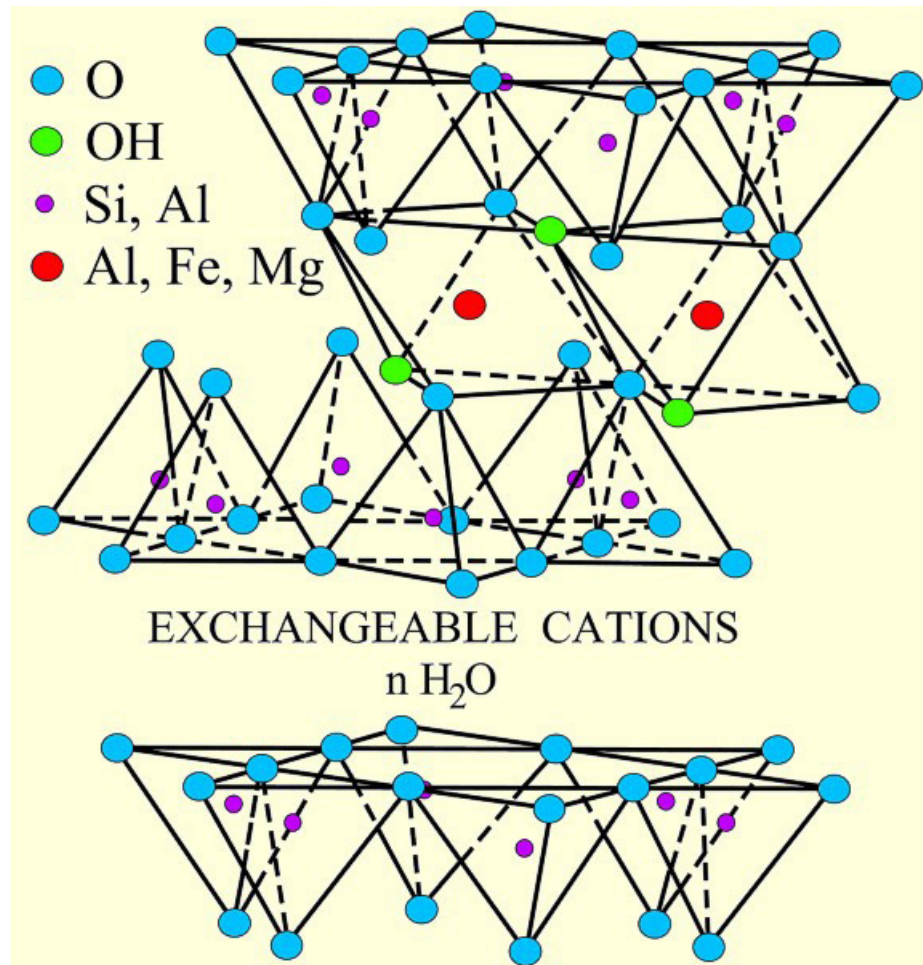


Fig. 10 The Montmorillonite structure [15]

Saponite and Hectorite

Saponite, a high magnesium smectite, is similar in structure to talc (with the trioctahedral magnesia layer sandwiched between the silica layers) but with limited substitution of tetrahedral Si^{4+} by Al^{3+} , while hectorite has the talc structure but with limited substitution of Li^+ for octahedral Mg^{2+} and partial substitution of lattice hydroxyls by fluorine. As with montmorillonite, the resulting charge imbalance is compensated by Na^+ or Ca^{2+} residing with oriented water in the interlaminar spaces. Saponite and hectorite have swelling, ion exchange, and absorbent properties similar to those of montmorillonite.

2.1.3 The Illite group

The Illite clays have a structure similar to that of Muscovite, but is typically both deficient in alkalis and have less Al^{3+} as substitution for Si^{4+} . The structure of Muscovite is complicated because of containing strongly covalent and strongly ionic interactions. The double formula $\text{K}_2\text{Al}_4[(\text{OH})_4|\text{Al}_2\text{Si}_6\text{O}_{20}]$ is shown in the Fig. 11. So-called 2:1 layers are composed of $\text{Si}_2\text{O}_5^{-2}$ and $(\text{Al},\text{Si})\text{O}_6$ groups connected by rigid covalent bonds. In the tetrahedron layers 1/4 of the Si^{4+} they are replaced by Al^{3+} . The negatively charged layer packages $\text{Al}_2(\text{OH})_2[\text{AlSi}_3\text{O}_{10}]$ are held together by K^+ ions. The strength of the ionic bonding depends on isomorphous substitutions in the 2:1 layers [29],[35].

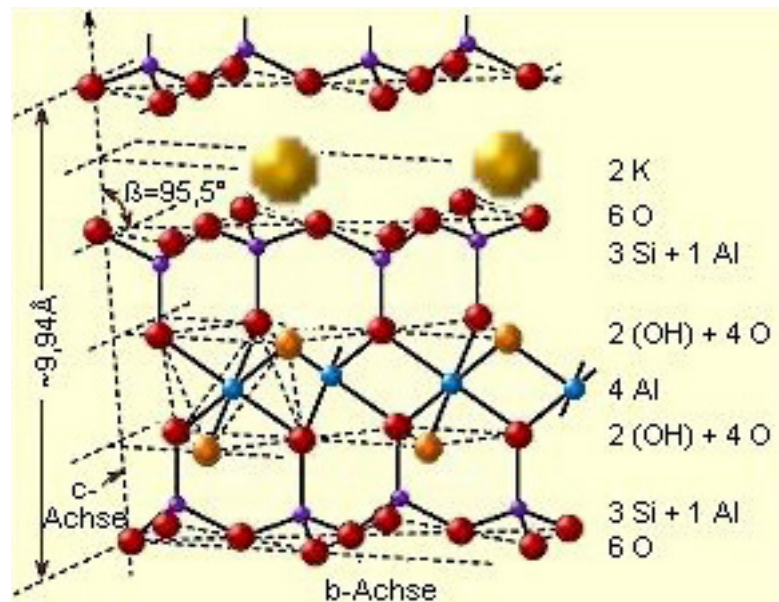
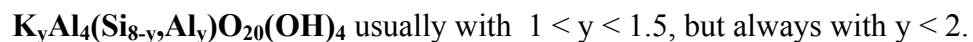


Fig. 11 The crystal lattice of Muscovite [35]

Thus, the general formula for the Illites is:



Because of possible charge imbalance, Ca^{2+} and Mg^{2+} ions can sometimes substitute for K^+ ions. The K^+ , Ca^{2+} or Mg^{2+} interlayer cations prevent the entrance of H_2O molecules into the structure. Thus, the Illite (shown on the Fig. 12) clays are non-expanding clays.

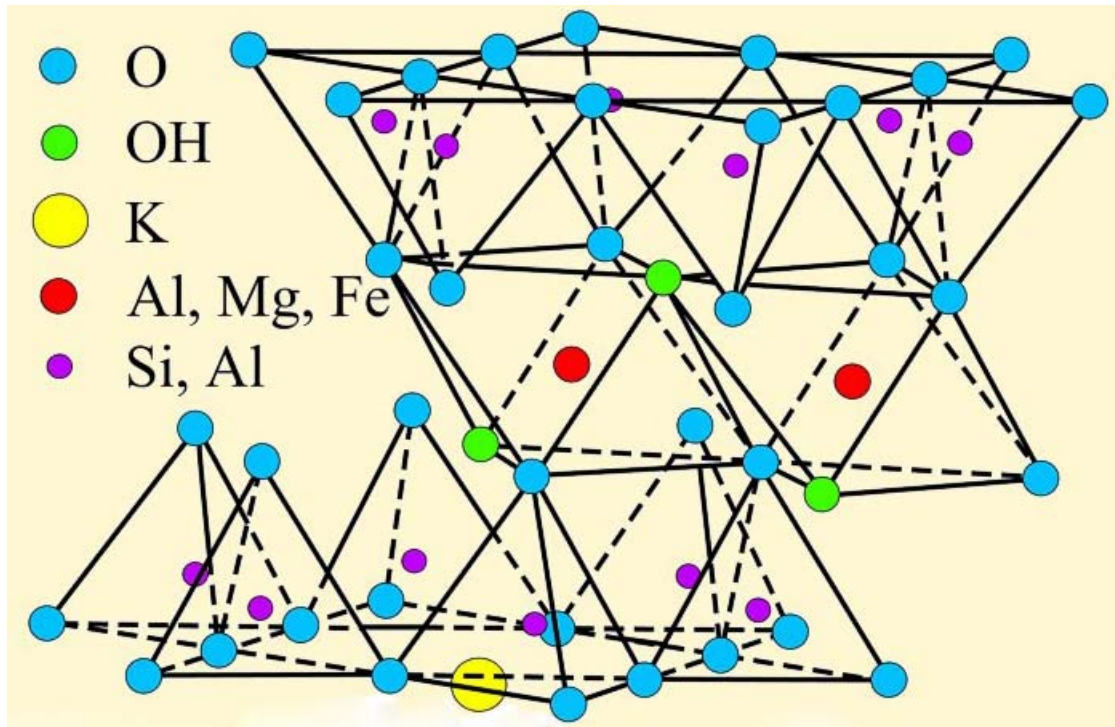


Fig. 12 The structure of Illite [15]

Illite clays are formed from weathering of K and Al-rich rocks under high pH conditions. Illite clays are the main constituent of ancient mud-rock and shales. [13] Illite is the common constituent in shales and is used as filler and for drilling mud [11].

2.1.4 The Chlorite group

In certain situations the 2:1 clay mineral can crystallize in an environment containing an excess of aluminium ions. Under these conditions an extra aluminum octahedral layer (Gibbsite) can be formed between the micelles. This formation is not random, but can be found as the complete layer in each intermicelle space. Minerals having this characteristic constitution are known as the *CHLORITE* group. The Gibbsite layer has the effect of binding the micelles tightly and this group of minerals is also non-expanding [12].

The Chlorite can have a rather complicated formula - $(\text{Mg,Fe,Al})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_6$ [13].

This group of minerals consists of alternate 2:1 micelles and Gibbsite layers. So, they are called the chlorites 2:1:1 mineral. The Gibbsite layer is in the integral part of the micelle, so the chlorites are also known as 2:2 minerals. Regardless of what they may be called, however, the repeat structure consists of the 2:1:1 or 2:2 combinations. The structure of Chlorite can be seen in the Fig. 13.[12].

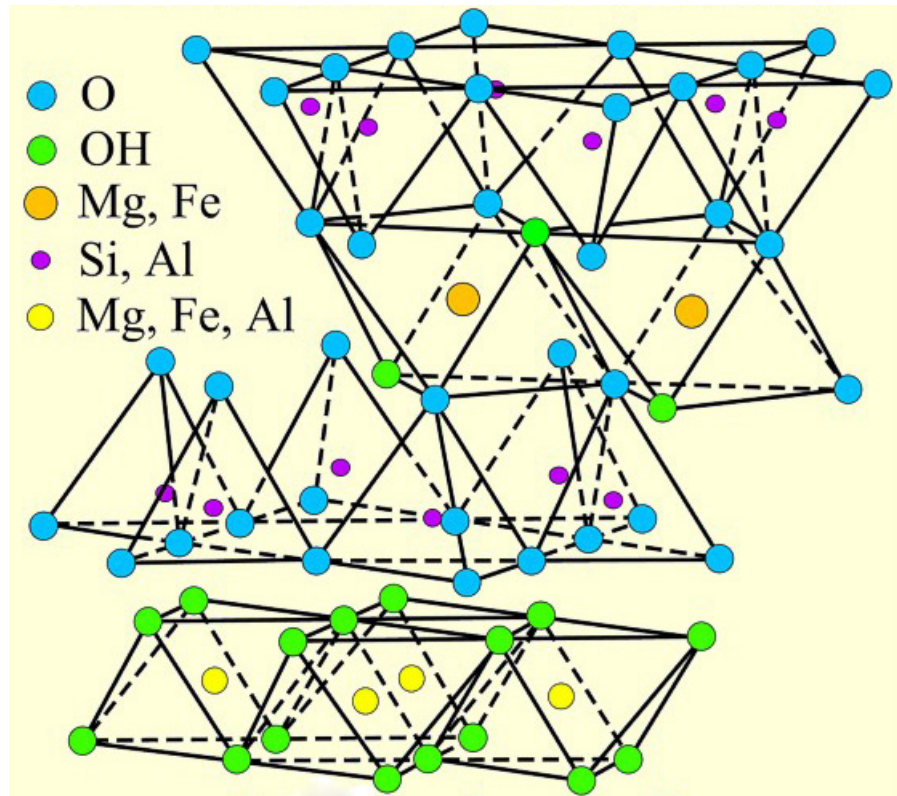


Fig. 13 The Chlorite structure [15]

Members of the chlorite group include:

1. The dioctahedral chlorite: Donbassite
2. The di,triocahedral chlorite: Cookeite, Sudoite
3. The trioctahedral chlorite: Clinocllore, Chamosite, Nimitite [30].

The various members are differentiated by the kind and amount of substitutions within the brucite-like layer [hydroxide sheet or interlayer sheet] and the tetrahedral and octahedral positions of the talc-like layer [2:1 layer]. The chlorite minerals are common components of low-grade green schist facies of metamorphic rocks, and of igneous rocks as hydrothermal alteration products of ferromanganese minerals. Chlorites are also constituents of argillaceous sedimentary rocks where these minerals occur in both detrital and authigenic forms [15].

2.1.5 Sepiolite and Palygorskite

Sepiolite (see Fig. 14) and palygorskite (see Fig. 15) have similar fibrous or lath-like morphologies. Palygorskite exhibits more structural diversity and, although both minerals are Mg silicates, has less Mg^{2+} and more Al^{3+} ions than sepiolite. The structures of both

minerals are similar in that tetrahedra pointing in the same direction form 2:1 ribbons that extend in the direction of the a-axis and have the average b-axis width of three linked tetrahedral chains in sepiolite (see Fig. 16) and two linked chains in palygorskite (see Fig. 17). Rectangular channels, which contain some exchangeable Ca^{2+} and Mg^{2+} cations and zeolitic water*, lie between the ribbons, and molecules of bound water lie at the edges of the ribbons.

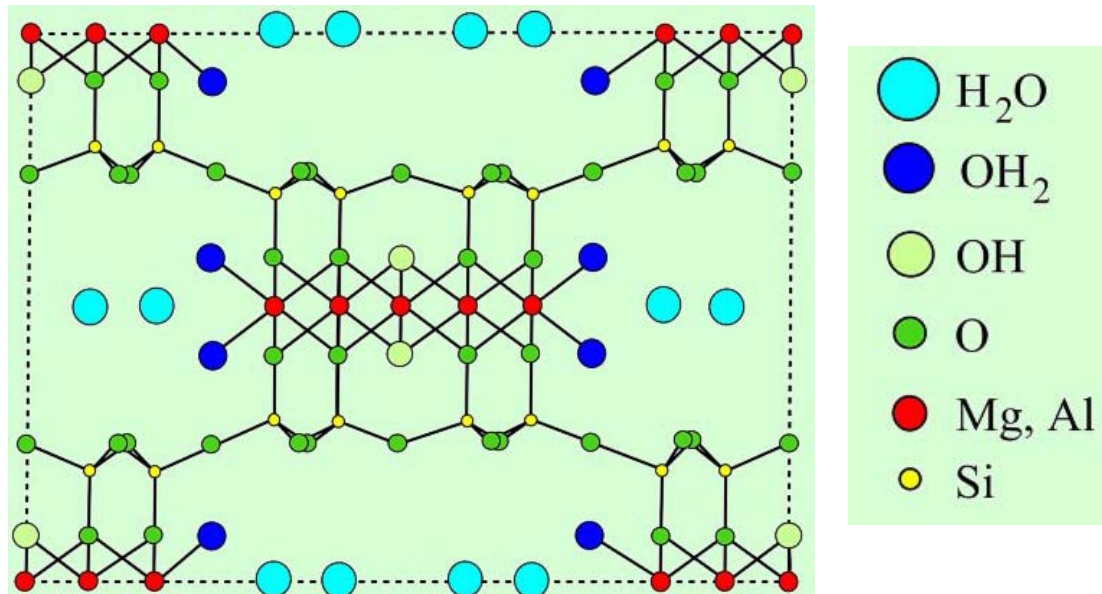


Fig. 14 The structure of Palygorskite [15]

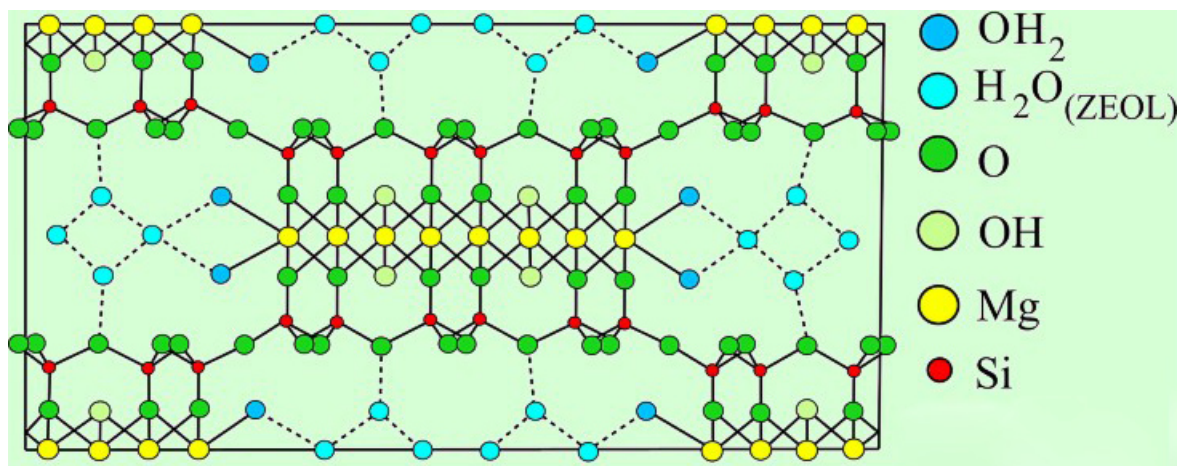


Fig. 15 The structure of Sepiolite [15]

* Zeolitic water comes and goes without affecting the structure of the original mineral (any of numerous hydrated aluminosilicate minerals, usually containing sodium, potassium, or calcium) If the structure is affected by dehydration, the water was not zeolitic, it was merely loosely held by the structure. If the mineral hydrates/dehydrates, back and forth, without changing the structure, the water is zeolitic.

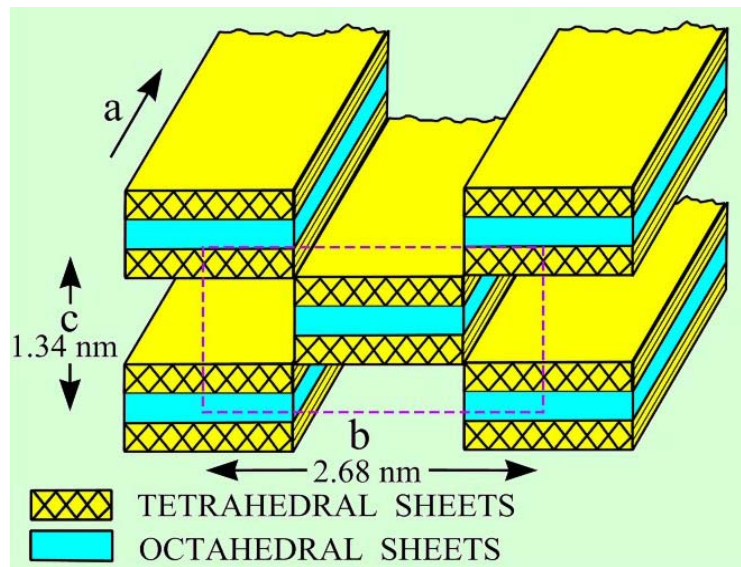


Fig. 16 The Sepiolite's structure [15]

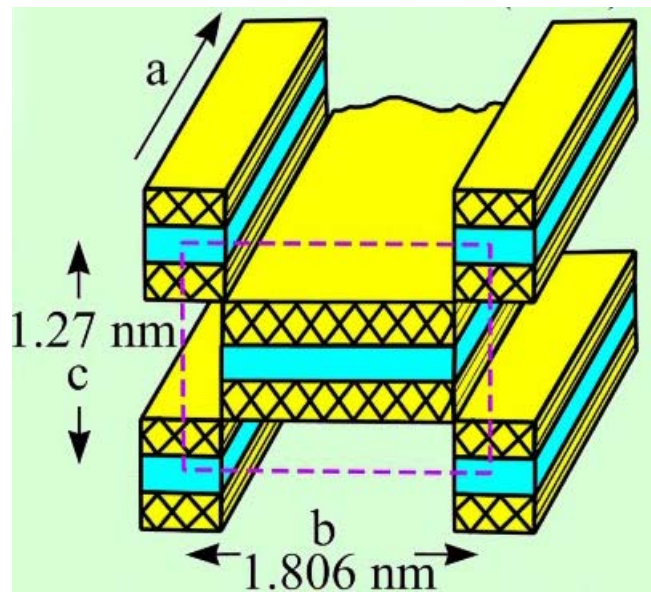


Fig. 17 The Palygorskite's structure [15]

Both sepiolite and palygorskite require alkaline conditions and high Si^{4+} and Mg^{2+} ions activities for stability. They are also loosely associated with low latitudes and semi-arid climates. Most major deposits were originally formed in shallow seas and lakes as chemical sediments or by the reconstitution of smectites, in open oceans by the hydrothermal alteration of volcanic materials, and in calcareous soils by direct

crystallization. Owing to their absorptive properties, sepiolite and palygorskite are used commercially as carriers, fillers, clarifying agents, and for lubricant reclamation [15].

2.1.6 Mixed-Layered Clays

Mixed-layer clay minerals are materials in which different kinds of clay layers alternate with each other. The mixing or interstratification in vertical stacking can be regular (ordered), segregated regular, or random (see Fig. 18). Commonly described mixed-layer clays include: illite-vermiculite, illite-smectite, chlorite-vermiculite (corrensite), chlorite-smectite, and kaolinite-smectite. Mixed-layer clays can be formed by weathering involving the removal or absorption of cations, hydrothermal alteration, or removal of hydroxide interlayers, and, in some cases, may represent an intermediate stage in the formation of swelling minerals from non-swelling minerals or visa versa [13],[15].

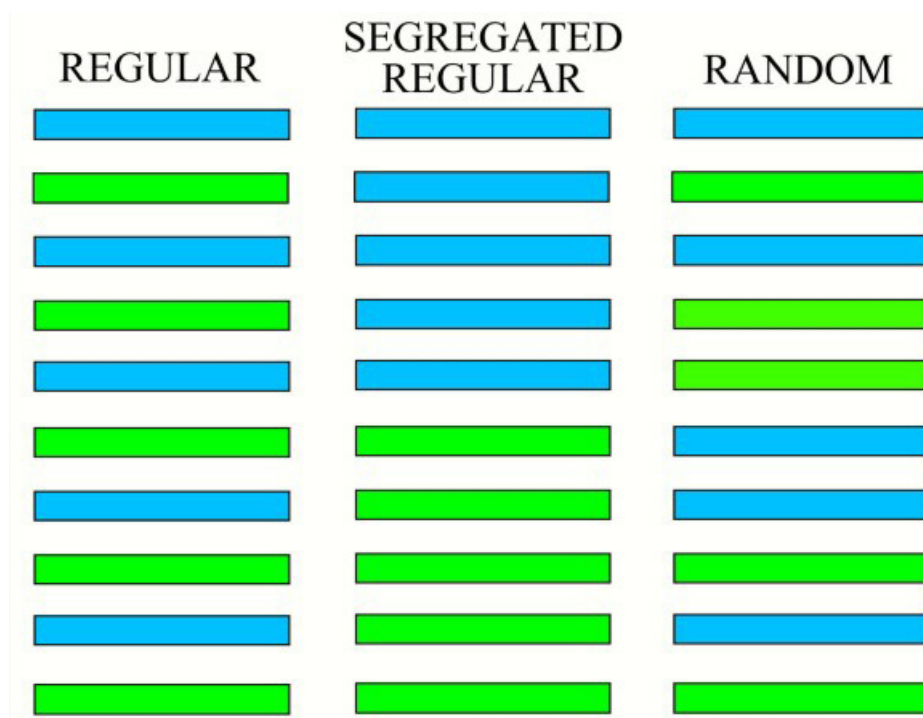


Fig. 18 The Mixed-Layered clays [15]

2.1.7 Vermiculite

Vermiculite is trioctahedral 2:1 clay. The individual vermiculite particle is composed of the octahedral magnesia layer sandwiched between two tetrahedral silica layers. There can be some substitution of iron and aluminum ions for magnesium ions in the octahedral layer. On the other hand, there is always some substitution of aluminum ions for silicon

ions in the tetrahedral layer, creating a charge imbalance. Vermiculite layers are separated by two oriented water layers, between which magnesium cations reside to balance the charge on the mineral lattice. Because of the separation of platelets by the oriented water, the magnesium ion is not fixed but exchangeable for other cations (see the structure in the Fig. 19). This ion exchange capacity is exploited in certain industrial applications. The layers are electrically neutral and interlayer cations occupy only about one-third of the available sites, cohesion between the layers is typically weak.

The approximate chemical formula for the vermiculite is:

$[\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2][\text{Mg}_{0.5}(\text{H}_2\text{O})_y]$, where the first set of brackets denotes the host layer, while the second the guest layer, and the hydration state is variable.

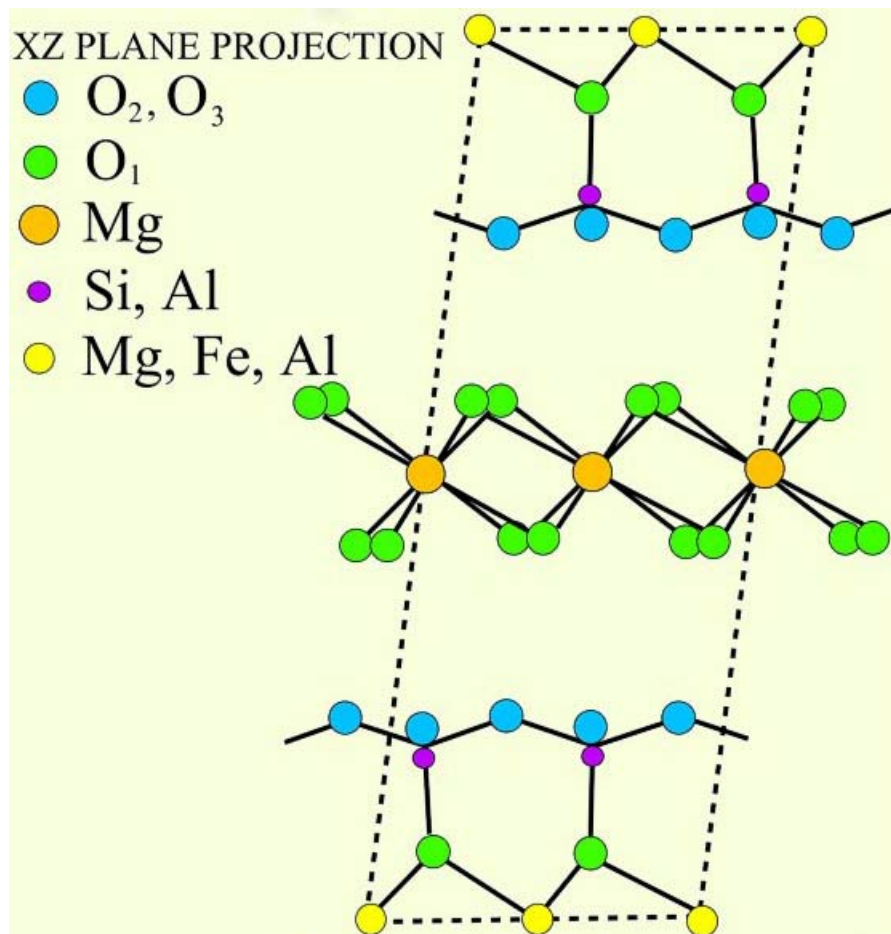


Fig. 19 The structure of Mg-Vermiculite [15]

Vermiculite is also hydrated and less expansible than smectite because of its relatively high charge. Moreover, vermiculite can not readily incorporate additional layers of water between platelets and therefore can not be completely delaminated in aqueous systems.

Vermiculites are usually formed in sediments by the alteration of micaceous minerals (biotite and chlorite to trioctahedral vermiculite; muscovite to dioctahedral vermiculite). However, vermiculites formed through the alteration mica are comparatively rare in marine sediments. Marine vermiculites are probably derived from volcanic material and chlorite. [15], [20],[21],[23].

2.2 The utilization of some clay nanofillers

The most commonly studied nanofillers among the others are the clay nanofillers. The montmorillonite (MMT) is the most widely utilized clay because of its large cation exchange capacity. However, there are new types of nanofillers, which have been developed recently [25].

2.2.1 Kaolinite

The structure of kaolinite was described in paragraph 2.1.1.

There are many descriptive classifications of kaolin products and they are in certain cases specific to particular markets. The most common designations are as follows:

Primary (residual) kaolin – this term is in reference to geologic origin, it means that the clay occurs in the deposit where it is formed.

China clay – this is a ceramics industry term synonymous with what is today called simply kaolin. China clay is substantially pure white or near-white kaolinite characterized by low plasticity, low strength, and good fired whiteness.

Ball clay – in the ceramics industry ball clay is the highly plastic, fine-grained sedimentary clay containing 70% kaolinite. Ball clay is characterized by the presence of organic matter, high green strength, and light fired colour.

Calcined clay – the kaolin, usually water-washed soft clay is calcined to either partially or totally in order to remove surface hydroxyl groups.

Surface-treated clay – this is the processed kaolin that has been surface modified (e.g., with stearates or silanes) to improve compatibility with and performance in organic matrices.

The best known and most highly utilized deposits of kaolin are in the Cornwall area of south-western England, in Georgia and South Carolina in the United States, and in the

lower Amazon region of Brazil. Extraction of the original Sedlec/Zettlitz deposit (quarry near the village Sedlec, now the part of Karlovy Vary) ended up in 1962. The currently extracted quarries are located within 20 km north and west of Karlovy Vary [31].

The kaolinite is the very common material in earth and is widely used as raw material in several industrial sectors. It can be used as the functional filler and extenders in paint, plastics, rubber, and ink.

Today is kaolinite used as new nanofiller, because is cheaper then minerals of smectite group. For example the EVOH (ethylene-vinyl alcohol copolymers) kaolinite nanocomposites were obtained as new material with enhanced barrier properties for food packaging applications. In this case natural kaolinite clay was used and generated as a recyclable residue of the spray-dried process commonly used in the tile industry [25].

The largest use of kaolin in plastics is for production of calcined kaolin. This type of kaolin is mainly used in PVC wire insulation to improve electrical resistivity. Calcined kaolin is also used in agricultural polyethylene films to improve their infrared absorption characteristics and in engineering resins. It is used in both silane-treated and untreated forms, for improving of physical properties and heat deflection. Both air-float and water-washed, fine-particle size kaolin is used in thermosets to provide a smooth surface finish, reduced cracking, warping and crazing, and to obscure fiber reinforcement patterns.

Delaminated clays improve thermoplastic physical properties, including enhanced impact resistance when surface treated [20],[22],[25].

Sedlecký Kaolin a.s. products fillers for plastics in our country, that names are OT 76M, MKM.

The kaolinite clay used in the article [25] was the natural kaolinite that was supplied by the company Arciblansa in Alcora (Spain). Authors didn't report more information about name of this kaolinite.

Kaolinite is important in the production of ceramics and porcelain. However, the greatest demand for kaolinite is in the paper industry to produce a glossy paper using in most magazines [16].

2.2.2 Vermiculite

The structure of vermiculite was described in the paragraph 2.1.7.

The major mines are located in South Africa, China, Brazil, Zimbabwe, and the United States. Today the largest operating mines are located in the Palabora region of North-Eastern Transvaal in South Africa, in the northwestern corners of China, and along the eastern Appalachian range in the United States (Virginia and South Carolina). [14],[27].

Vermiculite has larger cation exchange content (CEC) (100–150 meq/100g) than montmorillonite (70-130 meq/100g). The properties of 90% of used vermiculite are the low-density, expanded form. Commercial vermiculite is differentiated according to whether or not it has been exfoliated.

Vermiculite concentrate – Since the objective of nearly all vermiculite production is the expanded form, the principal product of vermiculite mining is a vermiculite concentrate. Vermiculite ores typically contain only about 35% of vermiculite. The equilibrium may consist of the various proportions of mica, chlorite, and other sheet silicates. The ore is beneficiated to vermiculite flake concentrates have at least 90% purity realized by either dry or wet processes. Vermiculite concentrates are supplied to regional plants which carry out the thermal exfoliation that result in the expanded products. Vermiculite concentrates are screened and sold under various grade designations based on relatively narrow particle size distributions. Flakes that are less than 60 meshes are too fine for exfoliation and are discarded during beneficiation.

Expanded vermiculite – Expanded vermiculite has a very low bulk density. Exfoliation is carried out in regionally located plants in order to minimize the high cost of transportation to customers per unit weight of product. Vermiculite concentrates are expanded in furnaces by quick exposure (0.25–8 seconds) at 900°C or more. The heat turns rapidly the interlayer water to steam, which pushes the individual vermiculite laminate apart. The vermiculite increases in volume by 8-20 times and decreases in bulk density by 85-90 m⁻³. There are 90% entrapped air by volume % in the expanded particles and thereby these particles possess excellent insulation properties. The expanded material is separated from nonexpanding impurities by air classification and is either bagged directly or ground to sizes suitable for various applications. If vermiculite is properly exfoliated, its expanded form retains 90-95% of ion exchange capacity.

Chemically exfoliated vermiculite – Vermiculite can be chemically delaminated by treating an aqueous dispersion and alternately with the brine solution and the n-butylammonium solution. The mineral's exchangeable magnesium cation is sequentially replaced by sodium and the alkylammonium cation. This leads to increases the interlayer separation sufficiently to allow the osmotic entry of water. The mineral thus expands to form an aqueous gel. This gel is used to coat glass fibres and fibreglass fabrics, thereby doubling their effective working temperature [20]. The hydrogen oxide exfoliation of vermiculite was related to the separation of silicate layers with oxygen formed by the decomposition of peroxide and to the disruption of the equilibrium between the layers and the interlayer cations due to vigorous release of hydroxide groups from the structure [33].

The using of vermiculite comes out from ability to strongly expand by heating to temperature 700 – 900°C. Vermiculite has some interesting properties which make it useful in the number of industrial applications. It is lightweight, fireproof, non-toxic and non-hazardous. It can be produced in a number of different sizes, and expanded to different densities. Moreover, it can hold water, and other liquids such as oils, nutrients, chemical mixtures, and special coatings [27]. It is generally used as packaging material for anti-shocking. Vermiculite is recognized as a material particularly suited for fire protection. Vermiculite - based products range from factory made boards and panels to premixed coatings suitable for application by mechanical spray or by hand plastering techniques. A whole new family of vermiculite products can be generated by varying the chemical process. It is possible to produce flexible films, papers and coatings, and make specialized additives for various industries. Developments in this area of research have indicated that it may be feasible to manufacture complex silicate structures which, when polymerized, would form inorganic analogues of organic polymer systems with unique properties of flexibility and fire resistance [34].

2.2.3 Montmorillonite

Montmorillonite is the main constituent of Bentonite, derived by weathering of volcanic ash. Deposits are found in Italy, Greece, Cyprus, the Philippines, South Africa, Brazil, England, Japan, Romania, Germany, Mexico, Argentina, Spain, India, Hungary, Poland, Canada, Turkey, Florida, Georgia, Illinois, and Texas.

Because of MMT hydrophilicity, it is used as a drilling mud (to keep drill holes open), and for plugging leaks in soil, rocks, and dams. The separation of the unit layers into almost unit cell thicknesses is useful for application in plastic industry. These extremely thin, platy particles can be exchanged using organic molecules interacting with the plastic polymers to produce very strong and heat resistant products. These nano-particles are currently utilized in certain automotive plastic components and in plastic food wrappings and packaging. [5],[6],[13],[20],[22].

There are two particular characteristics of layered silicates that are generally considered for PLS (polymer layered silicates) nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the aptitude to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are interrelated since the degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation [6].

The leading suppliers of clay filler for nanocomposites are Southern Clay Products (Cloisite), Nanocor and Süd-Chemie (Nanofil).

2.2.4 Hectorite

Hectorite is also typically used in the most demanding of coatings applications. For automotive coatings, hectorite is particularly important because it can provide extraordinary thixotropy to keep the spray coating under challenging rheological conditions. Hectorite clay can be synthesized in the production setting. The innovation has addressed the issues of water demand, the ease of dispersion and the rate of activation [26]. In the future, the research of M.P.Eastman and T.L.Porter will be directed towards developing MALDI techniques for characterizing the organic and biopolymers formed on hectorite and other clays, learning how to build robust clay-polymer based chemical sensors, characterizing new polymeric materials formed in the confines of the clay interlayer and exploring sample reaction for biomolecules on clay surfaces. Present indications are that such research will significantly increase the scientific and practical significance of clay-polymer composites [4].

2.3 The properties of clay nanofillers

Clay/polymer nanocomposites offer tremendous improvement in a wide range of physical and engineering properties for polymers with low filler loading. This technology can now be applied commercially and has received great attention in recent years.

2.3.1 The advantages of clay nanofiller

The nanofillers can improve these characteristics in filled polymer:

- *Enhancement of mechanical properties e.g. strength, modulus and dimensional stability*

A wide range of engineering properties can be significantly improved with a low level of filler loading, typically less than 5 wt%. Polymers such as nylon-6 show an increase in Young's modulus of 103%, in tensile strength of 49%, and in heat distortion temperature of 146% [2]. They generally exhibit improved mechanical properties compared to conventional composites, because reinforcement in the PLS (polymer layered silicate) nanocomposites occurs in 2D rather than 1D, and no special processing is required to laminate the composites [6].

- *Thermal stability and heat distortion temperature*

The thermal degradation of PMMA intercalated within montmorillonite can be delayed under conditions that completely degraded virgin PMMA. With a filler content of just 10 wt. %, the degradation temperature was 40-50°C higher than for virgin PMMA. Achieving a significant improvement in thermal stability through low filler content in nanocomposites is particularly attractive because end-products can be made cheaper, lighter and easier to process [32]. In addition Heat Distortion Temperature was shown to increase from 65°C for the unmodified polyamide to 152°C for the nanoclay-modified material, all the above being achieved with just a 5% loading of montmorillonite clay [24].

- *Flame retardancy and reduced smoke emissions*

Traditional commercially available flame retardants such as aluminium trihydrate or halogen-containing compounds are highly effective. However, the mechanical properties and processing of flame retardant polymers are often negatively

influenced by the large quantities of halogen-free flame retardants that are needed. The addition of many flame retardants often increases the production of carbon black and carbon monoxide during combustion. Nanocomposites have many advantages over these traditional flame retardants; they contain no additional halogen and are considered as an environmentally-friendly alternative.

The flame retardancy mechanism of layered silicate nanocomposites is based on the char formation and its structure. The char insulates the base polymer from heat and forms a barrier, reducing the escape of volatile gases from the polymer combustion. Although still a relatively new area of development, nanocomposites based on layered silicates as fillers are highly important as a new system for flame retardant polymers with improved properties. It can be used for polymers PP, PS and PA-6 [32].

- o *The decrease of permeability to gases, water and hydrocarbons*

The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be substantial. Data provided from various sources indicates oxygen transmission rates for polyamide-organoclay composites which are usually less than half that of the unmodified polymer [24].

- o *Chemical resistance*

The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. Data provided by De Bievre and Nakamura of UBE Industries reveals significant reductions in fuel transmission through polyamide-6/66 polymers by incorporation of a nanoclay filler. As a result, considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars [24].

- o *Optical clarity in comparison to conventionally filled polymers*

The thickness of individual clay layers is much smaller than the wavelength of visible light so that well exfoliated clay/polymer nanocomposites should be optically clear [2].

o Other advantages

PLS nanocomposites may be utilized as unique model systems to study the states and dynamics of polymer chains in confined environments, which are fundamental to many industrially important fields, including tribology, adhesion, fabrication, and catalysis [6].

2.3.2 The disadvantages of clay nanofillers

To date one of the few disadvantages associated with nanoparticles incorporation has concerned toughness and impact performance. Some of the data presented has suggested that nanoclay modification of polymers such as polyamides could reduce impact performance. Clearly this is an issue which would require consideration for applications where impact loading events are likely. In addition, further research will be necessary to, for example, develop a better understanding of formulation/structure/property relationships, better routes to platelet exfoliation and dispersion etc. [24]. The other major difficulties facing the development of clay/polymer nanotechnology are the lack of understanding of the mechanisms of the enhancement effect, the difficulty in application to thermosetting polymers, and the lack of thermally stable organoclays [2]. Intercalation of clays with the precursor of a thermosetting polymer can change the functionality of the polymer. It is well known that the major engineering properties of thermosetting polymers are a function of the extent of cross-linking. Nevertheless, there have been reports of improvements in mechanical properties of low extent cross-linked thermosetting polymer systems such as epoxy resin with low T_g and polyurethanes. However, little progress has been made with high extent cross-linked polymer systems. The last difficulty is directly concerned with the commercialization of clay/polymer nanotechnology, i.e. the lack of commercially available and thermally stable organoclays. Most commercially available organoclays are produced by the exchange of metal cations in clay galleries with organic ammonium salts. These ammonium salts are thermally unstable and can degrade at temperatures as low as 170°C. Clearly, such surfactants are not suitable for most engineering plastics when applying melt processing technology to produce nanocomposites. Although many thermally stable surfactants have been identified, such as phosphonium, these surfactants are too expensive for commercial use. New initiatives are moving toward direct modification of hydrophilic clays using multifunctional polymers and oligomers to produce thermally stable organoclays for polymer/clay nanocomposites.

2.3.3 The application in past and in the future

Such mechanical property improvements have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial applications. The first commercial application of these materials was the use of clay/nylon-6 nanocomposites as timing belt covers for Toyota cars. After this, Untika introduced nylon-6 nanocomposites for engine covers on Mitsubishi's GDI engines. Noble Polymers had developed clay/polypropylene nanocomposite for structural seat backs in the Honda Acura. In addition to automotive application, polymer/clay nanocomposites have been used to improve barrier resistance in beverage applications. Honeywell has developed commercial clay/nylon-6 nanocomposite products, Aegis NC resin, for drink packaging applications. More recently, Mitsubishi Gas Chemical and Nanocor have co-developed Nylon-MXD6 nanocomposites for multilayered polyethylene terephthalate bottle application.

These nanocomposite materials include potential for utilization as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc. Nanoclay/polymer composites are currently showing considerable promise for food packing (for example a non-refrigerated packaging system capable of maintaining food freshness for three years) [2] ,[24].

CONCLUSIONS

Significant progress in the development of polymer/clay nanocomposites has been made over the past one and a half decades.

Clay was chosen as filler due to its low loading range. The smectite clays such as montmorillonite are the most important filler system in the field of polymer-clay nanocomposites. However lately other clays such as hectorite, kaolinite have been used as nanofillers [25],[26]. The ability of these clays to organize and direct polymer synthesis is rooted in a number of unique structural and chemical properties.

Several methods have been developed to produce polymer/clay nanocomposite, among the most investigated belongs: in-situ polymerization, the solution induced intercalation, melt intercalation and template synthesis. The melt intercalation is the most common because neither a suitable monomer nor a compatible polymer-silicate solvent system is always obtainable.

This Bachelor thesis contains the description of the other types of clay nanofillers than only commonly using montmorillonite. So, it deals mainly with kaolinite, vermiculite, hectorite and saponite. The reason of this is that each of them has a specific utilization in many industrial branches.

Their using has both many advantages and disadvantages. The addition of clay nanoparticles not only can improve the mechanical properties, but also can have positive effects on the thermal stability. Moreover, there are other improvements in physical and engineering properties if the clay nanofillers are used such as fire retardancy, barrier resistance and ion conductivity. Finally, the optical properties of the polymer are not significantly affected by the inclusion of nanofiller. On the other hand, it is necessary to understand the mechanism of the major engineering properties enhancement to can tailor the composites nanostructure so that particular engineering properties were achieved. Majority of clay nanofillers can be intercalated and exfoliated, but some of them only in some measure with the modifiers.

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