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# **Polymeric Nanocomposite Materials**

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# 1. Introduction

Nowadays the enormous use of polymer materials is attributed to their extraordinary combination of properties, low weight and ease of processing. However for improvement of some properties such as thermal and mechanical stability, large numbers of additives were added to polymeric matrix and formed polymer matrix composite [1, 2].

A composite is defined as a combination of two or more materials with different physical and chemical properties and distinguishable interface. Composite materials have a wonderful and different range of applications. Important advantages of composites over many metal compounds are high specific stiffness and specific strength, high toughness, corrosion resistance, low density and thermal insulation [1-3].

In most composite materials, one phase is usually continuous and called the matrix, while the other phase called the dispersed phase. On the basis of the nature of the matrices, composites can be classified into four major categories:

- 1. Polymer matrix composite
- 2. Metal matrix composite
- 3. Ceramic matrix composite
- 4. Carbon matrix composite [4].

Polymer matrix composite can be processed at a much lower temperature, compared to other composite. Depending on the types of polymer matrices, polymer matrix composite are classified as thermosetting composites and thermoplastic composites [4].

# 2. Polymer matrix nanocomposite

Scientists for improve the properties of composite materials investigate composites with lower and lower fillers size, leading to the development of microcomposites and the recent trend in composite research is nanocomposites. Nanocomposites refer to composites in which one phase has nanoscale morphology such as nanoparticles, nanotubes or lamellar nanostructure [1-5].

The improvement of the properties by the addition of particles can be achieved when:

- a. Adequately good interaction between the nanoparticles and the matrix
- b. Good dispersion of particles within the matrix.

In nanocomposites, covalent bonds, ionic bonds, Vander Waals forces, hydrogen bonding could exist between the matrix and filler components [3,4].

# 2.1 Classification of nanocomposite

One of the classifications is based on the nanomaterial's dimensional morphology.

- 1. Zero dimensional nanomaterial such as nanoparticle [6-8].
- 2. One dimensional nanomaterial such as nanowire and nanotube [9]
- 3. Two dimensional nanomaterial such as silicate layers
- 4. Three dimensional nanomaterial such as zeolites [10-12]

# 2.2 Classification based on kind of synthesis procedure

- 1. Direct incorporation of nanoscale into a polymer melt or solution, such as addition several type metal oxide and hydroxide to polymeric matrix [5].
- 2. In situ generation of nanoscale building blocks in a polymer matrix (reduction of metal ions in polymer matrix) [5].

For example for synthesis of polyaniline/cadmium sulfide, polyaniline was dissolved in dimethyl formamide solution. Then dimethyl cadmium was added and simultaneously H<sub>2</sub>S was passed through solution (Fig1) [13].

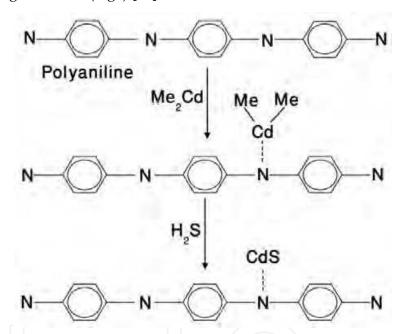


Fig. 1. Poly aniline/cadmium sulfide nanocomposite

- 3. Polymerization of monomers in the presence of nanoscale building bloks, such as polymerization of methyl metha acrylate or styrene in present nanoparticles [5].
- 4. A combination of polymerization and formation of nanoscale building blocks (for example intercalation of monomers into layered structures followed by polymerization) [5]. When a material structure has one dimension less than 100 nm, usually appear totally different behavior of its material properties, the properties of nanomaterials can sometimes produce an inverse transition of a property.

# 3. Some application of polymer matrix nanocomposite:

# 3.1 Flame retardant nanocomposite

Together with numerous advantages that synthetic polymeric materials provide to society in everyday life, there is one obvious disadvantage related to the high flammability of many

synthetic polymers. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications. Nanocomposites are very attractive due to the fact that small amount of nanostructure can lead to great improvement in fire resistant property of nanocomposite.

# 3.2 Nanocomposite with high mechanical stability, stiffness, strength, toughness

By using minimal addition levels, can be achieved excellent mechanical properties. For example polyamide-6clay nanocomposite, containing 5% clay, shows an increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength and 126% in flexural modulus [14].

# 3.3 Nanocomposite solar cells

Polymer-based solar cells have the capability of being used to make cheap large flexible panels. The only downside is substantially low efficiency compared to commercial solar cells [15]. Cadmium chalcogenides such as CdS nanoparticles in polymers have been used to make solar cells. Numerous efforts are being taken to improve the efficiency of the cells. In general a higher density of the nanoparticles is advantageous. Control of the band edge of the particles is also very important factor controlling the efficiency of the solar cell. Polymer-semiconductor nanocomposites offer the promise of a new generation of hybrid materials with numerous possibilities of applications such as in optical displays, catalysis, photovoltaics, gas sensors, electrical devices, mechanics, photoconductors and superconductor devices [15].

# 3.4 Nanocomposite membrane for gas separation and gas permeability

Many inorganic filler have dispersed in polymer matrices to improve pure polymeric membrane properties and constituted mixed-matrix membranes (MMMs). Result of such mixed matrix membrane is to the superior transport properties. With addition of low amount of nanoparticles to polymeric membrane, we achieved great increasing in permeability of membrane. There are many reports of improved penetrate permeability [16].

# 3.5 Nanocomposite with gas barrier performance

By addition alumina silicate layers to polymer matrix can be obtained gas barrier performance for nanocomposite.

# 4. Determination of the morphology of nanocomposites

As the nanocomposite properties dramatically depend on the good dispersion of the filler in the matrix, it is necessary to develop technical methods to characterise the nanodispersion. For determination of morphology, polymer matrix nanocomposite were characterized by some techniques such as transmission electron microscopy, TEM, scanning electron microscopy, SEM, atomic force microscopy, AFM and X-ray diffraction, XRD.

# 4.1 Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

SEM determined morphology and shape of surface of material, in polymer matrix nanocomposite especially when low amount of nanoparticles is added to polymer, polymeric chains cover the nanoparticle, thereupon in surface image of SEM, cannot be

determined nanoparticles in matrix. However when high percent of nanoparticles is added to polymer, usually can be seen nanoparticles in matrix. One way for determined of nanoparticles in polymeric matrix is using cross sectional SEM image, for preparation images of cross section of polymeric nanocomposite, a small amount of sample was immersed in liquid nitrogen for nearly some minute to ensure it was completely frozen. It was then removed from the liquid nitrogen and immediately was broken. AFM also determined surface of thin film sample, and in high loading nanoparticle, can be detected fillers in polymeric matrix. For example SEM images of tin and bismuth sulfide nanostructure and polymer matrix nanocomposite of those with acrylonitrile butadiene styrene (ABS) copolymer are shown in Fig 2, that confirm SEM images cannot perfectly determine nanoparticles in polymer matrix[17,18]. Also AFM images of pure copolymer and ABS/tin sulfide are shown in Fig 3, which shows the same results.

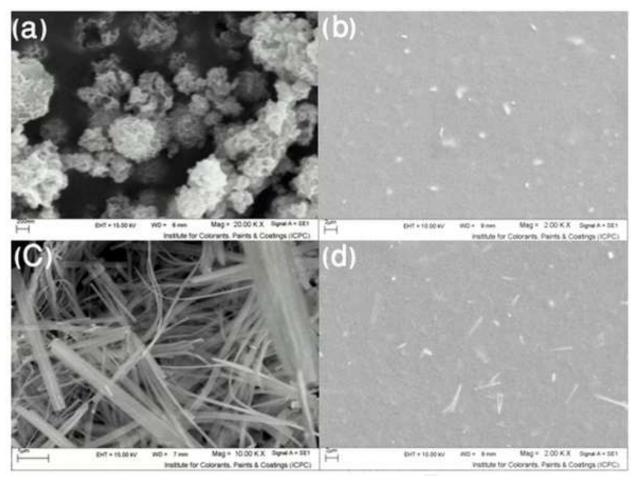


Fig. 2. SEM images of a) SnS nanoflowers b) ABS/SnS c) Bi<sub>2</sub>S<sub>3</sub> nanorods d) ABS/Bi<sub>2</sub>S<sub>3</sub> ref:17, 18

# 4.2 X-Ray Diffraction (XRD) technique

XRD enables the determination of the *d*-spacing of the clay. An immiscible system is obtained if the *d*-spacing in the presence of the polymer is unchanged from that of the pristine clay. If the *d*-spacing increases, this indicates that intercalation has occurred. Since the registry between the clay layers is lost in an exfoliated system, no peak is expected. Unfortunately, this same situation will occur if the clay has extensively disordered, so XRD

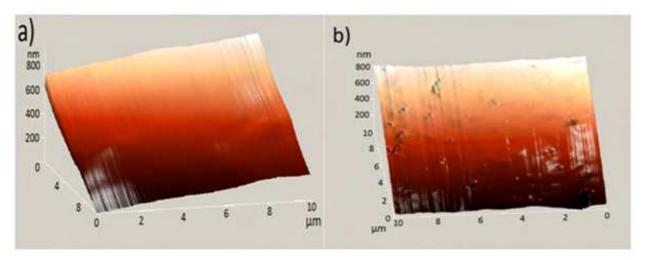


Fig. 3. AFM images of a) pure ABS b) ABS/SnS nanocomposit

information alone is not enough to identify the morphology. For these reasons, in general, XRD analysis is not used alone in studies to deduce the nanocomposite morphology [14]. XRD pattern ABS-clay hybrid nanocomposites are shown in Fig 4. With exchange Na<sup>+</sup> by alkyl ammonium, distance between layers increase and XRD peak shift to lower angle. XRD patterns of ABS-OMMT because of intercalation of single chains of ABS in the galleries of the host shows an increasing interlayer distance and peak shift to lower angle [19].

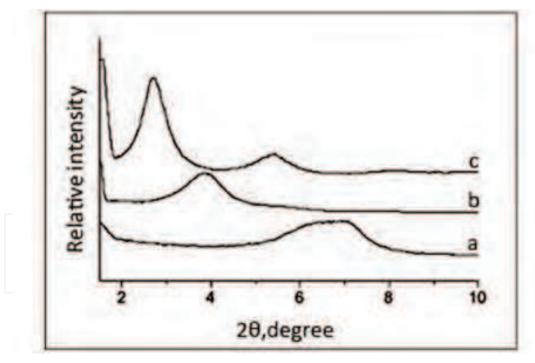


Fig. 4. XRD patterns of a) pristine sodium montmorillonite b) modified montmorillonite (OMT) c) ABS/OMT nanocomposite. ref:19

# 4.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is widely employed, in its simplest bright-field mode, as a tool for direct visualization of the nanocomposite structure of polymer nanocomposites. This is possible because there exists sufficient contrast for the transmitted

electrons between the polymer matrix and most filler (inorganic material such as metal oxides). In the extreme case, high-resolution TEM can even provide a qualitative picture of the inorganic filler crystal structure [20]. One must remember that to obtain one TEM requires only a miniscule piece of material and one cannot be certain that this is representative of the whole. The morphology can only be clearly determined by either sampling enough of the material [14]. Fig 5a shows TEM image of PMMA/TiO2 and TEM image of ABS/clay is shown in Fig 5b [19, 21].

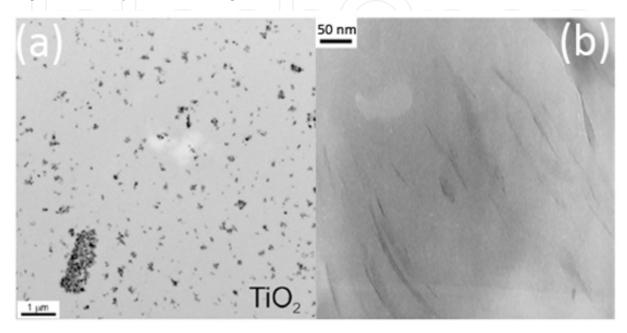


Fig. 5. TEM images of a) PMMA/TiO $_2$  nanocomposite b) ABS/OMMT nanocomposite ref:19,21

# 5. Flame retardancy

Flammability of polymers is one of their unpleasant properties that most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications Flame retardation is a process by which the normal degradation or combustion of polymers is altered by addition of certain chemicals. Various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment. The combined challenge thus consists in developing effective and environmentally friendly flame retardant systems for polymer materials. Most researches have been done for improving thermal stability by addition of nanoparticles [20, 22]. Any type of inorganic filler, even inert, can influence the reaction of polymers to fire for several reasons:

- 1. Reduction of content of combustible products
- 2. Changing the viscosity of the resulting material
- 3. Modification the thermal conductibility of the resulting material [22].

All these actions have an indirect incidence on the polymer's fire performance. Nevertheless, some minerals are more specifically used as flame retardants owing to their behavior at high temperature [22].

# 6. Some of laboratory fire testing

# 6.1 ThermoGravimetric Analysis (TGA)

TGA is an experimental technique in which the weight of a sample is measured as a function of sample temperature or time. The sample is typically heated at a constant heating rate. The results of a TGA measurement are usually displayed as a TGA curve in which percent weight is plotted against temperature. Different effects can cause a sample to lose, or even gain, mass, these include the following:

- 1. Evaporation of volatile constituents; such as desorption of gases and moisture
- 2. Thermal decomposition in an inert atmosphere with the formation of gaseous products
- 3. Oxidation of constituents[23].

TGA are often equipped with DTA (differential thermal analysis). In addition to showing the energetic nature of weight loss events, the DTA signal can also show thermal effects that are not accompanied by a change in mass, e.g. melting, crystallization or a glass transition [23].

# 6.2 Limited Oxygen Index: LOI

LOI is one of the most important and representative parameter for describing the flameretardant properties of plastics because of it is relatively simple method. The measurement consists of determining the minimum concentration of oxygen in a nitrogen-oxygen mixture that will sustain combustion. The higher LOI better the flame retardant property. This does not mean that a material with a high oxygen index will not burn; the test measures the ease of extinction of the fire [22].

The value of the LOI is defined as the minimal oxygen concentration  $[O_2]$  in the oxygen/nitrogen mixture  $[O_2/N_2]$ , As air contains 21% oxygen, materials with an LOI below 21 are classified as "combustible" whereas those with an LOI above 21 are classified as "self-extinguishing", because their combustion cannot be sustained at ambient temperature without an external energy contribution [22].

# 6.3 Differential scanning calorimetry: DSC

DSC is the most widely used of the thermal techniques available to the analyst and provides a fast and simple method for obtaining beneficial information about a material. A DSC analyzer measures the energy changes that occur as a sample is heated, cooled or held isothermally. The energy changes enable the user to find and measure the transitions that occur in the sample quantitatively such as measurement of glass transitions [23].

# 6.4 Cone calorimeter

Cone calorimeter is one of the most effective medium-sized polymer fire behavior tests. The cone calorimeter measures the rate at which heat is released in a fire. This instrument calculate the quantity of heat released per unit of time and surface area: HRR (heat release rate) expressed in kW/m2. The evolution of the HRR over time, in particular the value of its peak (pHRR), is usually taken into account in order to evaluate the fire properties [22]. Currently, numerous fire retardant fillers for the preparation of polymer nanocomposites

Currently, numerous fire retardant fillers for the preparation of polymer nanocomposites have been proposed, some famous flame retardant are:

# 7. Polymer/metal sulfide nanocomposite

With incorporation of a variety of nanoparticles in the polymer matrices, nanocomposites are much different from the conventional composites. Exfoliated metal sulfide filler particles

have significant barrier effect to slow down product volatilization and thermal transport during decomposition of the polymer, which assists composites with high thermal stability. For example influence of the content of cadmium sulfide (CdS) on the thermal degradation of poly styrene/ cadmium sulfide composites were examined [24]. TG curves (Fig 6), shows that thermal stability of PS/CdS composites is higher than in pure PS. Improved thermal stability of composites with respect to the pure PS can be assigned to partially altered molecular mobility of the polymer chains due to their adsorption on the surface of the filler particles. Simultaneously, adsorption of polymer chains onto the surface of CdS filler particles results in restriction of segmental mobility and serves to suppress chain transfer reactions. Polymer adsorption on the surface of filler particles is a crucial step for explanation of changed thermal stability of polymer/metal sulfide composites [25, 26]. Much effort has been made to develop novel methods to prepare nanostructured metal chalcogenide. Hydrothermal method and thermal decomposition provides a more promising way for the synthesis of crystals due to its low cost, high efficiency and potential for large-scale production [27-34].

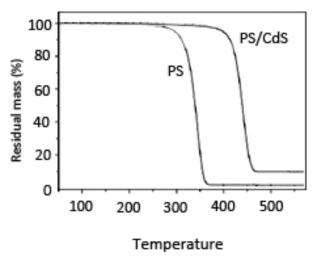


Fig. 6. TGA curves of pure poly styrene and polystyrene/cadmium sulfide nanocomposite from ref:24

# 8. Polymer/metal hydroxide nanocomposite

The most commonly used mineral flame retardants are metal hydroxides (The two most commonly used products are aluminum hydroxide and magnesium hydroxide). These material are used in wire , cables , poly(vinyl chloride) , polyethylene, various elastomers , phenolics, epoxies, and unsaturated polyesters. As the temperature rises, aluminum hydroxide decomposes endothermically and therefore absorbs energy. Moreover, they release non-flammable molecules (H<sub>2</sub>O, CO<sub>2</sub>), which dilute combustible gases upon heating at about 220°C with an endotherm of 1.17 kJ/g, whereas MH starts releasing water at about 330°C with an endotherm of 1.356 kJ/g [20]. Since both anhydrous alumina and magnesia are white highly refractory powders, they provide heat insulation by reflecting heat when they accumulate on a surface these flame retardants can also promote the formation of a protective ceramic or vitreous layer. To be used as polymer flame retardants, metal hydroxides need to decompose endothermically and release water at a temperature higher than the polymer processing temperature range, and around the polymer decomposition temperature [20].

The fire properties of ATH-filled polymers are only interesting at high loading levels. To pass flame retardancy tests, 35 to 65 wt% of metal hydroxide is required [20]. Increasing the loading of metal hydroxides will result in a significant loss in physical properties; therefore, the use of nanometric MDH and ATH can enable interesting fire performances to be achieved at lower loading levels. The enhancement of flame retardancy by nanosized Mg(OH)<sub>2</sub> was attributed to the good dispersion of the nanoparticles, which leads to the formation of more compact and cohesive char during the combustion test [35].

# 9. Polymer/metal and metal oxide nanocomposite

Filler particles have significant barrier effect to slow down product volatilization during decomposition of the polymer, which assists composites with high thermal stability. Adsorption of polymer chains onto the surface of filler particles results in restriction of segmental mobility and serves to suppress redistribution and chain transfer reactions [24]. Beside current famous flame retardant additives, many researches have been done about effect of metal oxide and metal nanoparticle to thermal property of polymers. In recent years, synthesis of transition metal nanoparticles is a growing research field in chemical science [36-39]. Metal particles have attracted considerable attention because of application in modern technologies. Metal oxide nanoparticles can be obtained by several methods, via a sol-gel technique a hydrothermal, sonochemistry and co-precipitation method [40-46]. For examples effectiveness of several type of metal oxide such as silica, ferric oxide, titanium oxide and copper oxide for improve thermal property of polymer matrix were surveyed [47-49]. For example influence of the content of ferric oxide and titanium oxide on the thermal degradation of poly methyl methaacrylate was examined. TGA curves, shows that thermal stability of nanocomposites is higher than in pure polymer (Fig7) [21]. Improved thermal stability of composites can be assigned to partially alter molecular mobility of the polymer chains due to their adsorption on the surface of the filler particles [24].

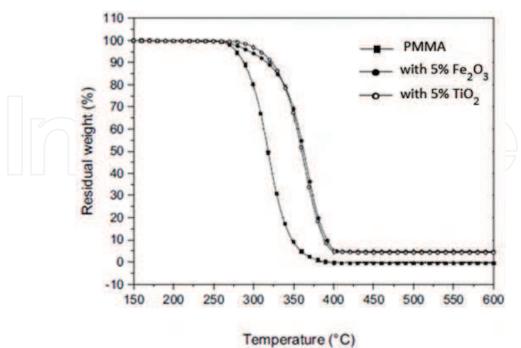


Fig. 7. TGA curves of pure PMMA and PMMA/metal oxide nanocomposite ref: 21

# 10. Polymer/layered silicate nanocomposite

The formation of well-dispersed polymer nanocomposites leads to modification of the degradation pathway of polymers and this clearly affects the fire behavior of nanocomposites. The currently accepted explanation for enhanced fire properties is that the clay forms a barrier to mass transport and which also insulates the underlying polymer from the heat source (Fig8) [20].

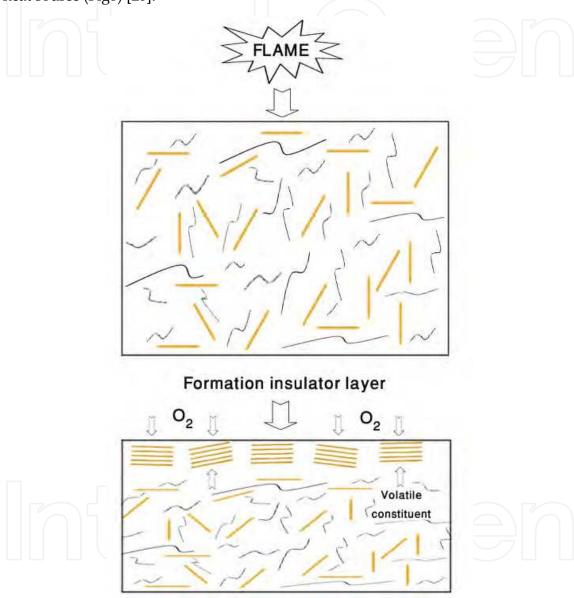
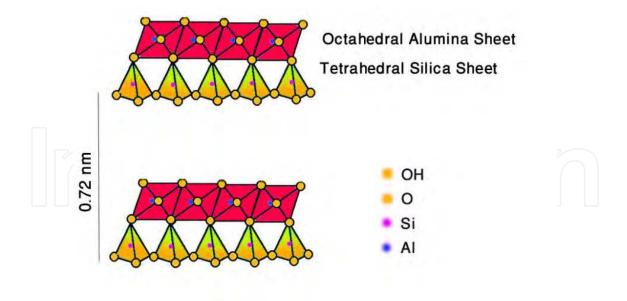


Fig. 8. Formation of insulator layer in polymer/clay nanocomposite

# 10.1 Crystal structures of some major clay minerals 10.1.1 Kaolinite

Kaolinite is called a 1:1 type of layered mineral that is composed of a tetrahedral silica sheet and an octahedral alumina sheet. The tetrahedral and octahedral sheets are connected with shared oxygen atoms (Fig 9). The charge within the layers is nearly balanced, and the chemical formula is  $Al_4[Si_4O_{10}](OH)_8$  or  $2Al_2O_3.4SiO_2.4H_2O$  [50].



# Kaolinite

Fig. 9. Structure of kaolinite

# 10.1.2 Pyrophyllite

The formula for pyrophyllite is  $Al_4[Si_4O_{10}](OH)_2$ . Pyrophyllite has a 2:1 layer structure consisting of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of alumina (Fig 10) [50].

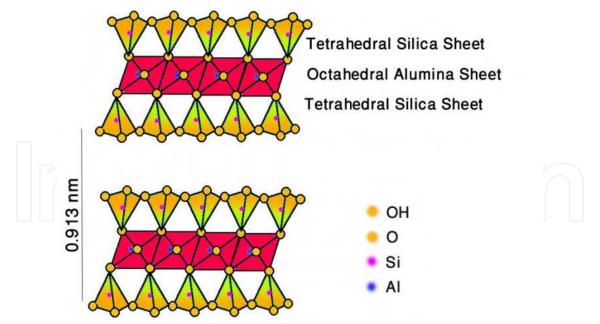


Fig. 10. Structure of pyrophilite

# **10.1.3 Montmorillonite**

The most promising candidate of the layered silicates is montmorillonite (MMT), owing to its natural abundance and high aspect ratio [51, 52]. MMT is a derivative of pyrophyllite.

The difference between the crystal structure of MMT and pyrophyllite is that the latter is neutral, while the former has layer charges due to isomorphic substitution. Substitutions occur in the octahedral sheet with Mg2+and Fe2+for Al3+ (Fig 11) [50].

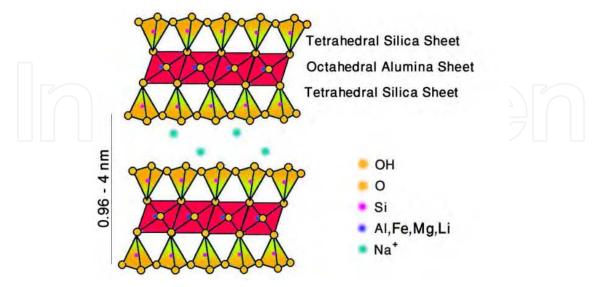


Fig. 11. Structure of sodium montmorillonite.

# 10.2 Organic clay modification

To make the silicate compatible with the polymer, the clay mineral is modified with an alkyl ammonium salt by cation exchange. Attractive interaction between the surfactant and the polymer greatly enhances the possibility of nano-dispersion of the clay within the polymer. Modification of Na<sup>+</sup> MMT with CTAB is shown in Fig 12.

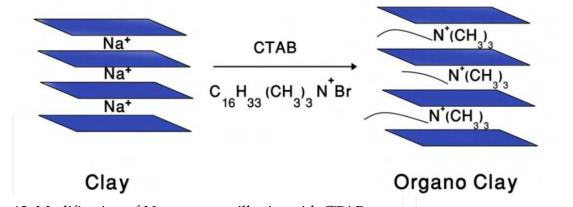


Fig. 12. Modification of Na+ montmorillonite with CTAB

If the polymer is unable to intercalate between the silicate sheets, the obtained composite can be considered as phase-separated composite. Beyond this classical family of composites when extended polymer chain is inserted in a crystallographically regular fashion between the silicate layers resulting in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers, the obtained composites can be called as 'intercalated nanocomposites. When the individual silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [53]. Different kind of interaction between polymeric chains and clay are shown in Fig 13 .Usually, the clay content of an exfoliated nanocomposite is much lower than that

of an intercalated nanocomposite. In the majority of the polymer nanocomposites formed, a combination of delamination and intercalation is obtained [54].

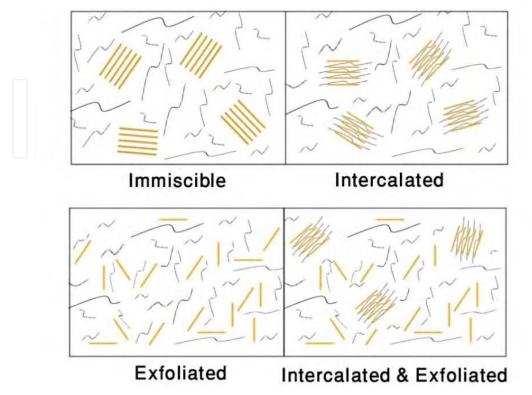


Fig. 13. Different kind of interaction between polymer and clay

# 11. Polymer/layered double hydroxide nanocomposite

Hydrotalcite compounds, known as layered double hydroxides (LDHs), belong to a class of anionic clay minerals. They have the general molecular formula [M2+1-x M3+x (OH)2]x+A n- x/n.mH2O, where M2+and M3+ are divalent and trivalent metal cations, such as Mg2+, Al3+, respectively, An- is an intercalated anion, such as CO32-, SO42-, and NO3-[55].

The majority of important applications are based on their permanent anion-exchange and adsorption capacity, the mobility of interlayer anions and water molecules, their large surface areas, and the stability and homogeneity of the materials formed by their thermal decomposition. Because of their highly tunable properties, LDHs are considered as a new emerging class of the most favorable layered crystals for preparing the multifunctional polymer/layered crystal nanocomposites [55].

When LDHs were added to a polymer matrix, the LDH releases the CO<sub>2</sub> gas and moisture, diluting the concentration of burning gas. In addition, MgO and Al<sub>2</sub>O<sub>3</sub> act as layers of heat insulation. The layer structure of LDH shows in Fig 14.

# 12. Halogen-containing flame retardant

For explanation of correlation between halogenated flame retardant and polymer matrix nanocomposite firstly we should explain synergistic effect concept:

A synergistic effect occurs when the combined effects of two chemicals are much greater than the sum of the effects of each agent given alone. Halogen-containing flame retardants

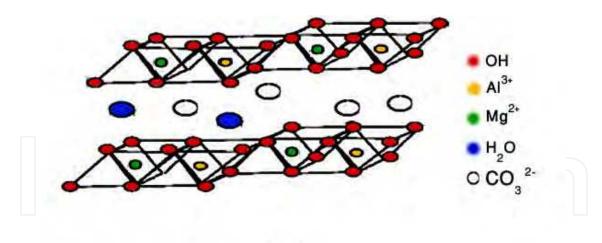


Fig. 14. Structure of layered double hydroxide

release halogen in the form of radical of halogen at temperature of decomposition of the polymer. Chlorine and bromine can be used as halogenated flame retardant. These halogens, because of their low bonding energy with carbon atoms, can readily be released and take part in the combustion process [20].

LDH

Very reactive free-radical species such as H and OH are very important for sustaining combustion. The hydrogen radical is responsible for the chain-branching free-radical reactions in the flame whereas the hydroxyl radical is responsible for the oxidation of CO to CO<sub>2</sub>, which is a highly exothermic reaction and is responsible for the larger part of the heat generation in the flame. The physical effect of halogen halides is comparable to that of inert gases, CO<sub>2</sub>, and water[20].

Sb<sub>2</sub>O<sub>3</sub> is synergistic with halogen-containing flame retardants because it facilitates delivery of halogen atoms in the gas phase and prolongs residence of the halogens in the flame zone so that more "hot" radicals can be scavenged. Antimony trioxide reacts with halogen containing compound, forming SbCl<sub>3</sub> or SbBr<sub>3</sub> [20].

The use of nanometric Sb<sub>2</sub>O<sub>3</sub> can enable interesting fire performances to be achieved at lower loading levels. The enhancement of flame retardancy by nanosized Sb<sub>2</sub>O<sub>3</sub> was attributed to the good dispersion of the nanoparticles, which leads to the formation of more compact and effective char during the combustion test.

# 13. Polymer/carbon nano tube nanocomposite

The investigation of carbon nanotubes (CNT) has opened a totally new window for the development of polymer matrix composites with novel properties and applications. The most widely studied nanofibrous materials with respect to polymer flame retardancy are carbon nanotubes (CNTs). The extremely low diameter of CNT and their high aspect ratio make them an ideal material to improve the properties of the polymer matrix. CNTs are an interesting alternative to the use of conventional flame retardants and nanoclays. Their incorporation at low loading rate (<3 wt %) has been reported to improve the flammability of a large range of polymers [5, 23]. For example TGA curve related to PMMA/CNT nanocomposite is shown in Fig 15. Initial degradation onset of pure PMMA and PMMA-SWNT are at 322 and 359 °C, respectively. So, relatively a small amount (0.5 wt %) of SWNT thermally stabilized the PMMA by around 37 °C [56].

#### 13.1 Treatment of carbon nanotubes

Functionalization of carbon nanotubes is an effective way to improve interaction between CNTs and polymer matrix. Treatment has been performed by oxidation using a mixture of sulfuric and nitric acid .The oxidized carbon nanotubes were then functionalized with different types of agents such as amines or SOCl<sub>2</sub> (Fig 16).The functionalization has been performed by refluxing a suspension of oxidized CNTs with the amine to ensure a quantitative conversion [57-61].

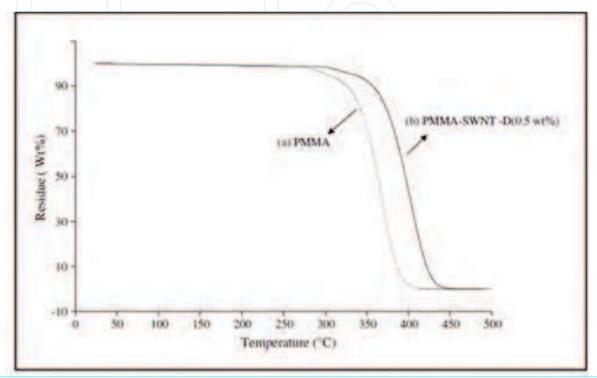


Fig. 15. TGA curves of a)PMMA b)PMMA/CNT nanocomposite ref:56

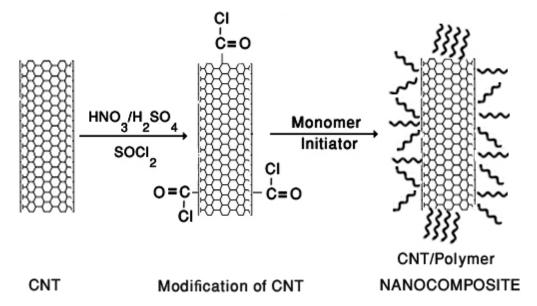


Fig. 16. Modification of carbon nanotube with organig agents

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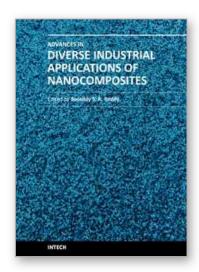
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# **Advances in Diverse Industrial Applications of Nanocomposites**

Edited by Dr. Boreddy Reddy

ISBN 978-953-307-202-9 Hard cover, 550 pages Publisher InTech Published online 22, March, 2011 Published in print edition March, 2011

Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

# How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Masoud Salavati-Niasari and Davood Ghanbari (2011). Polymeric Nanocomposite Materials, Advances in Diverse Industrial Applications of Nanocomposites, Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-202-9, InTech, Available from: http://www.intechopen.com/books/advances-in-diverse-industrial-applications-of-nanocomposites/polymeric-nanocomposite-materials

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