Chapter 1

Polymer/ Clay Nanocomposites: Concepts, Researches, Applications and Trends for The Future

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1. Introduction

On 29th December 1959, the physicist Richard Feynman delivered a lecture titled “There is plenty of room at the bottom” atthe American Physical Society. Such a lecture is a landmark of nanotechnology, asFeymann proposed the use of nanotechnology to store information as well as a series of new techniques to support this technology [1]. From then on, the technological and scientific mastership ofnanometric scale is becoming stronger due to the new research tools and theoretical and experimental developments. In this scenario, the worldwide nanotechnology market, in the next five years, is expected to be ofthe order of 1 trillion dollars [2].

Regarding polymer/ clay nanocomposite technology, the first mention in the literature was in 1949 and is credited to Bower that carried out the DNA absorption by the montmorillonite clay[3]. Moreover, other studies performed in the 1960s demonstrated that clay surface could act as a polymerization initiator [4,5] as well as monomers could be intercalated between clay mineral platelets [6]. It is also important to mention that, in 1963, Greeland prepared polyvinylalcohol/ montmorillonite nanocomposites in aqueous medium [7].

However, until the early1970s, the minerals were only used in polymers as fillers commercially aiming to reduce costs, since these fillers are typically heavier and cheaper than the added polymers. During the 1970s, there was a vertiginous and successive increase in thepetroleum price during and after the 1973 and 1979 crises [8]. These facts, coupled with polypropylene introduction in commercial scale, besides the development of compounds with mica, glass spheres and fibers, talc, calcium carbonate, led to an expansion of the ceramic raw materials as fillers and initiated the research as these fillers interacted with polymers.

Nevertheless, only in the late 1980swas the great landmark in the polymer clay nanocomposite published by Toyota regarding the preparation and characterization of polyamide 6/ organophilic clay nanocomposite to be used as timing belts in cars [9-11]. This new material, that only had 4.2 wt.%, had an increase of 40% in the rupture tension, 68% in the Young modulus and 126% in the flexural modulus as well as an increase in the heat distortion temperature from 65ºC to 152ºC in comparison with pure polymer [12]. From then on, several companies introducedthermoplastic nanocomposites, such as polyamide and polypropylene,inautomotive applications [13]. Another highlightedapplication is as gas barrier, by using polyamides or polyesters [14].

2. Definitions

2.1. Polymer/ clay nanocomposites

Polymer/ clay nanocomposites are a new class of composites with polymer matrix in which the dispersed phase is the silicate constituted by particles that have at least one of its dimensions in the nanometer range (10^{-9} m).

2.2. Clays

The mineral particles most used in these nanocomposites are the smectitic clays, as, for example, montmorillonite, saponite and hectorire [15,16]. These clays belong to the philossilicate 2:1 family and they are formed by layers combined in a sucha waythat the octadedrical layers that have aluminum are between two tetrahedrical layers of silicon (Figure 1). The layers are continuous in the *a* and *b* directions and are stacked in the *c* direction.

The clay thickness is around 1 nm and the side dimensions can vary from 30 nm to various micrometers, depending on the clay. The layer stacking by Van der Waals and weak electrostatic forces originates the interlayer spaces or the galleries. In the layers, aluminum ions can be replaced by iron and magnesium ions, as well as magnesium ions can be replaced by lithium ions and the negative charge is neutralized by the alkaline and terrous- alkalinecations that are between the clay layers. Moreover, between these layers, water molecules and polar molecules can enter this space causing an expansion in the *c* direction. This resulting surface charge is known as cation exchange capacity (CEC) and is expressed as mequiv/ 100g. It should be highlighted that this charge varies according to the layer and is considered an average value in the whole crystal [17-20].

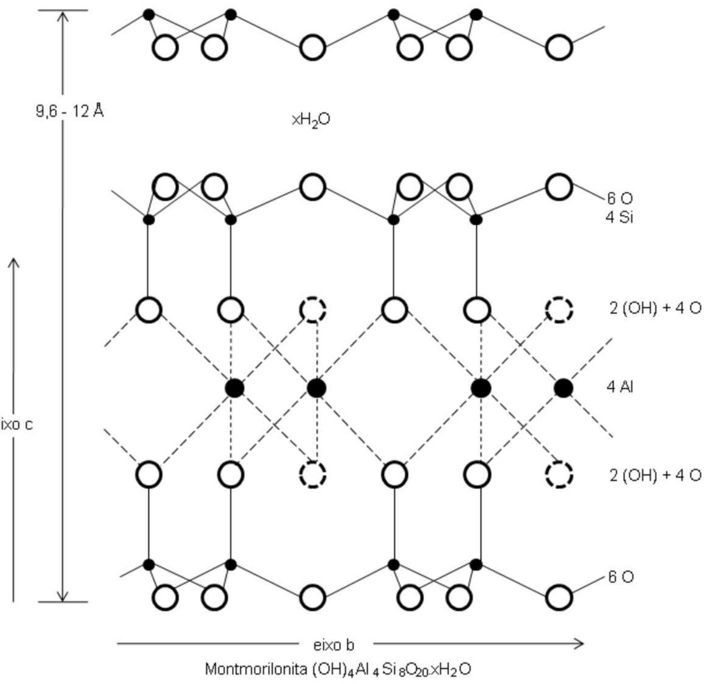

Figure 1. Schematic representation of montmorillonite.

2.3. Polymers

Polymers are constituted by largemolecules, called macromolecules, in which the atoms are linked between each other through covalent bonds. The great majority of the polymers are composed oflong and flexible chains whose rough sketch is generally made of carbon atoms (Figure 2). Such carbon atoms present two valence electrons notshared in the bonds between carbon atoms that can be part of the bonds between other atoms or radicals.

These chains are composed ofsmall repetitive units called *mero*. The origin of the word *mero*derives from the Greek word *meros*, which means part. Hence, one part is called by monomer and the word polymer means the presence of several *meros*.

When all the *meros* of the polymer are equal the polymer is a homopolymer. However, when the polymer is composed oftwo or more *meros*, the polymer is called copolymer.

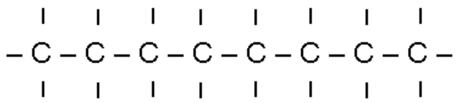

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Figure 2. Representation of an organic polymer chain.

Regarding the polymer molecular structure, polymers are linear when the *meros* are united in a single chain. The ramified polymers present lateral ramifications connected to the main chain. Polymers with crossed bonds have united linear chain by covalent bonds. Network polymers have trifunctional*meros* that have three active covalent bonds, forming 3D networks (Figure 3)

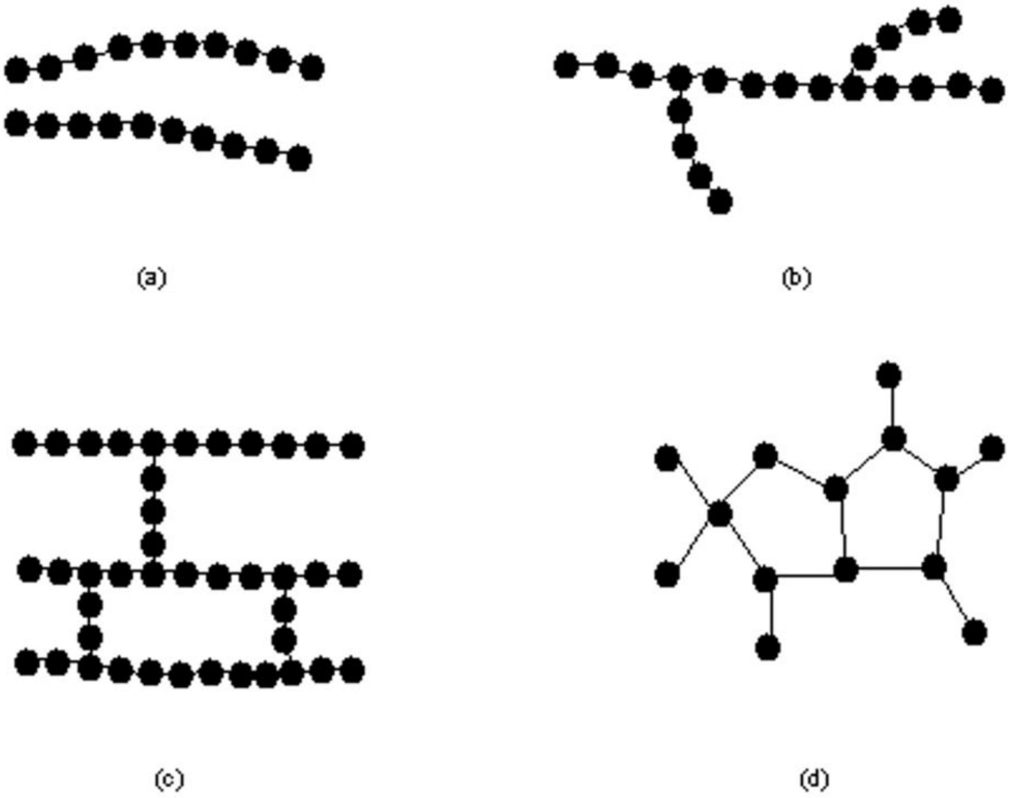


Figure 3. Schematic representation of: (a) linear, (b) ramified, (c) with crossed bonds and (d) network [21].

Polymers can be amorphous or semi-crystalline according to their structure. It is reasonable that the polymers that have a great number of radicals linked to the main chain are not able to have their molecules stacked as close as possible and, for this reason, the polymer chains are arranged in a disorganized manner, originating amorphous polymers. The polymers with linear chains and small groups are grouped in a more oriented form, forming crystals.

As a consequence of the polymer structure, there are two types of polymers: thermoplastic andthermofixes. Thermoplastic polymers can be conformed mechanically several times with reheating by the shear of the intermolecular bonds. Generally, linear and ramified polymers are thermoplastic and network polymers are thermofixes.

Thermofix polymers do not soften with temperature since there are crossed bonds in the 3D structure. Therefore, they cannot be recycled [21]

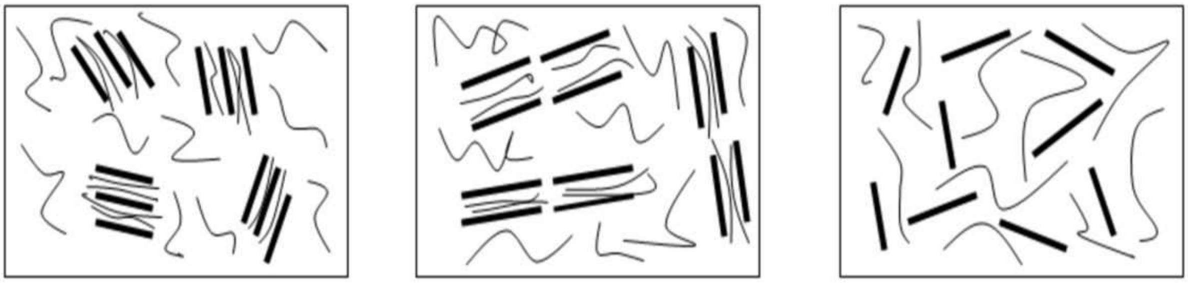
2.4. Polymer/ clay nanocomposite morphology

Depending on the interphase forces between polymer and clay, different morphologies are thermodynamically accepted (Figure4):

intercalated nanocomposite: the insertion of the polymer matrix in the silicate structure is crystalographicallyregular, alternating clay and polymer;

flocculated nanocomposites: it would be the same structure of the intercalated nanocomposite, except forthe formation of floccus due to the interaction between the hydroxile groups of the silicate;

exfoliated nanocomposites: individual clay layers are randomically separated in a continuous polymer matrix ata distance that depends on the clay charge [22,23]



intercalated

intercalated and flocculated

exfoliated

Figure 4. Polymer/ clay nanocomposites morphologies.

The formation and consequent morphology of the nanocomposites are related to entropic (ex.: molecular interactions) and enthalpic (changes in the configurations of the components) factors. Hence, efforts have been made to describe these systems. As an example, Vaia and Giannelis developed a model to predict the structure above according to the free energy variation of the polymer/ clay mixture in function of the clay layer separation.

The free energy variation, ΔH, associated to the clay layer separation and polymer incorporation is divided into two terms: the term related to the intern energy variation, ΔU, associated to the configuration changes of various components.

$$\Delta H = H(h) - H(h0) = \Delta U - T\Delta S \tag{1}$$

Where h and h_0 are the initial and final separation of the clay layers.Then, when $\Delta H<0$, the intercalation process is favorable.

Such model presents as a limitation the separation of the configuration term, theintermolecular interactions and the separation of the entropy terms of various components.

Other mathematical models were also developed for studies of simulation of the thermodynamics of the polymer/ clay nanocomposites. These models consider the nanocomposite thermodynamics and architecture, the interaction between clay and polymer to the free energy and the polymer and clay conformation.

Specifically for polyamide 6 and 66/ clay nanocomposites, the study of the molecular dynamics was employed, which uses the bond energy between the various components that composes the nanocomposite.

The kinetics of polymer/ clay nanocomposite formation is also a very important issue to predict the resulting nanocomposite. Studies of the molecular dynamics were also employed to understand the system kinetics. Other mathematical models were also used to describe the system kinetics, but kinetics is less understood than thermodynamics.

There is still the needof developing models that are explored in individual time and length scales, besides the integration of concepts that permeate from smaller to larger scales, that is, in the quantum, molecular, mesoscopic and macroscopic dominium [24].

2.5. Preparation methods of polymer/ clay nanocomposite

Three methods are widely used in the polymer/ clay nanocomposite preparation. The first one is the *in situ*polymerization in which a monomer is used as a medium to the clay dispersion and favorable conditions are imposed to carry out the polymerization between the clay layers. As clay has high surface energy, it performs attraction by the monomer units to the inside of the galleries until equilibrium is reached and the polymerization reactions occur between the layers with lower polarity, dislocating the equilibrium and then, aiming at the diffusion of new polar species between the layers.

The second method is solution dispersion. Silicate is exfoliated in single layers by using a solvent in which the polymer or pre-polymer is soluble. Such silicate layers can be easily dispersed in a solvent through the entropy increase due to the disorganization of the layers that exceed the organizational entropy of the lamellae. Polymer is then sorved in the delaminated layers and when the solvent is evaporated, or the mixture is precipitated, layers are reunited, filled with the polymer.

Moreover, there is also the fusion intercalation, amethod developed by Vaia et al. in 1993 [25]. In this method, silicate is mixed with a thermoplastic polymer matrix in its melted state. Under these conditions, the polymer is dragged to the interlamellae space, forming a nanocomposite. The driving force in this process is the enthalpic contribution of the interactions between polymer and clay.

Besides these three techniques, the use of supercritical carbon dioxide fluids and sol-gel technology can also be mentioned [26].

3. Polymer and clay modifications to nanocomposite formation

As explained before, the great majority of polymers are composed of a carbon chain and organic groups linked to it, thus presentinga hydrophobic character. On the other hand, clays are generally hydrophilic, making them, at a first view, not chemically compatible. Aiming to perform clay dispersion and polymer chains insertion, it is necessary to modify these materials.

There are two possibilities to form nanocomposites: clay organomodification that will decrease clay hydrophilicity and the use of a compatibilizing agent in the polymer structure, by grafting, to increase polarity. The concepts that govern each of these modifications will be explored in this chapter.

3.1. Clay organomodification

This method consists in the interlamellae and surface cation exchange (generally sodium and calcium ions) by organic molecules that hold positive chains and that will neutralize the negative charges from the silicate layers, aiming to introduce hydrophobicity and then, producing an organophilic clay. With this exchange, the clay basal space is increased and the compatibility between the hydrophilic clay and hydrophobic polymer. Therefore, the organic cations decrease surface energy and improve the wettability by the polymer matrix.

The organomodification, also called as organophilization, can be reached through ion exchange reactions. Clay is swelled with water by using alkali cations. As these cations are not structural, they can be easily exchanged by other atoms or charged molecules, whichare called exchangeable cations.

The greaterdistance between the silicate galleries due to the size of the alquilammonium ions favor polymer and pre-polymer diffusion between the galleries. Moreover, the added cations can have functional groups in their structure that can react with the polymer or even begin the monomer polymerization. The longerthe ion chain is and the higher the charge density is, the greaterthe clay layer separation will be [4,11].

3.2. Use of a compatibilizing agent

Generally, a compatibilizing agent can be a polymer which offers a chemically compatible nature with the polymer and the clay. By a treatment, such as the graftization of a chemical element that has reactive groups, or copolymerization with another polymer which also has reactive groups, compatibility between the materials will form the nanocomposite. Amounts of the modified polymer are mixed with the polymer without modification and the clay to prepare the nanocomposites.

Parameters such as molecular mass, type and content of functional groups, compatibilizing agent/ clay proportion, processing method, among others, should be considered to have compatibility between polymer and clay. Maleic anidride is the organic substance most used to compatibilize polymer, especially with the polyethylene and polypropylene, since the polar character of maleic anidride results in favorable interactions, creating a special affinity with the silicate surfaces [27,28].

4. The most important polymers employed in polymer/ clay nanocomposites

In this item, examples of studies about the most important polymers that are currently employed in the polymer/ clay nanocomposite preparation will be presented. Fora better understanding, polymers are divided into general-purpose polymers, engineering plastics, conductive polymers and biodegradable polymers.

4.1. General-purposepolymers

General-purpose polymers, also called commodities, represent the majority of the total worldwide plastic production. These polymers are characterized by being used in low-cost applications due to theirprocessing ease and low level of mechanical requirement. The formation of nanocomposites is a way to addvalue to these commodities.

4.1.1. Polyethylene (PE)

PE is one of the polymers that most present scientific papers related to nanocomposite formation. Maleic anidride grafted PE/ Cloisite 20A nanocomposites were prepared by two techniques: fusion intercalation and solution dispersion. Only the nanocomposites produced by the first method produced exfoliated morphology. The LOI values, related to the material flammability, were lower in all composites and were highly reduced in the exfoliated nanocomposites due to the high clay dispersion [29].

Another work presented the choice of a catalyzer being supported on the clay layers that are able to promote *in situ* polymerization, besides exfoliation and good clay layer dispersion. The organophilic clays (Cloisite 20A, 20B, 30B and 93A) were used as a support to the Cp_2ZrCl_2 catalyzer. The higher polymerization rate was obtained with Cloisite 93A and the clay layers were dispersed and exfoliated in the PE matrix [30].

4.1.2. Polypropylene (PP)

Rosseau et al. prepared maleic anidride grafted PP/ Cloisite 30B nanocomposites by water assisted extrusion and by simple extrusion. The use of water improved clay delamination dispersion and, consequently, the rheological, thermal and mechanical properties [29].

The use of carbon dioxide in the extrusion of PP/ Cloisite 20A nanocomposites enabled a higher separation between the clay layers. The use of clay at lower contents in the foam formation also suppressed the cell coalescence, demonstrating that the nanocomposite is also favorable to produce foams [31].

4.1.3. PVC

The use of different clays (calcium, sodium and organomodified montmorillonite, aluminum magnesium silicate clay and magnesium lithium silicate clay) was studied in the preparation of rigid foam PVC nanocomposites. Although the specific flexure modulus and the density have been improved by the nanocomposite formation, the tensile strength and modulus have their values decreased in comparison with pure PVC [32].

4.2. Engineering plastics

Engineering plasticsare materials that can be used in engineering applications, as gear and structural parts, allowing the substitution of classic materials, especially metals, due to their superior mechanical and chemical properties in relation to the general-purpose polymers [33]. These polymers are also employed in nanocomposites aiming to explore their properties to the most.

4.2.1. Polyamide (PA)

Among all engineering plastics, this is the polymer that presents the highest number of researches involving the preparation of nanocomposites. PA/ organomodified hectorite nanocomposites were prepared by fusion intercalation. Advanced barriers properties were obtained by increasing clay content [34]. The flexure fatigue of these nanocomposites were studied in two environments: air and water. It was observed that the clay improved this property in both environments [35].

4.2.2. Polysulfone (PSf)

PSf/ montmorillonite clay nanocomposite membranes were prepared by using solution dispersion and also the method most employed in membrane technology, wet-phase inversion. A hybrid morphology (exfoliated/ intercalated) was obtained, and itsdispersion was efficient to increase a barrier to volatilization of the products generated by heat and, consequently, initial decomposition temperature. By the strong interactions between

polymers and silicate layers, the tensile strength was increased and elongation at break was improved by the rearrangement of the clay layers in the deformation direction. Furthermore, hydrophobicity was also increased,so that membranes couldbe used in water filtration operations, for example [36].

4.2.3. Polycarbonate (PC)

By in situ polycondensation, PC/ organophilic clay exfoliated nanocomposites were prepared. Although exfoliated nanocomposites were produced, transparency was not achieved [37].

4.3. Conductive polymers

Conductive polymers, also called synthetic metals, have electrical, magnetic and optical properties that can be compared to thoseof the semiconductors. They are also called conjugated polymers, since they have conjugated C=C bonds in their chains which allow the creation of an electron flux in specific conditions.

The conductive polymer conductivity is dependent on the polymer chains ordering that can be achieved by the nanocomposite formation.

4.3.1. Polyaniline (PANI)

PANI is the most studied polymer in the polymer/ clay nanocomposite technology. Exfoliated nanocomposites wereprepared with montmorillonite which contained transition by *in situ* polymerization. The thermal stability was improved in relation to the pure PANIduethe fact thatthe clay layers acted as a barrier towards PANI degradation [38].

4.3.2. Poly(ethylene oxide) (PEO)

PEO nanocomposites werepreparedwiththreetypes of organophilicclays (Cloisite 30B, Somasif JAD400 e Somasif JAD230) by fusion intercalation. The regularity and spherulites size of the PEO matrix were altered by only using Cloisite 30B. An improvement in the storage modulus of the other nanocomposites was not observed since the spherulites were similar in the other nanocomposites [39].

4.4. Biodegradable polymers

Biodegradable polymers are those that, under microbial activity, have their chains sheared. To have the polymer biodegradabilization, specific conditions, such as pH, humidity, oxygenation and the presence of some metals were respected. The biodegradable polymers can be made from natural resources, such as corn; cellulose can be produced by bacteria from molecules such as butyric, and valeric acid which produce polyhydrobutirate and polyhydroxivalerate or even can derive from petroleum; or fromthe biomass/ petroleum mixture, as the polylactides [40].

4.4.1. Polyhydroxibutirate (PHB)

The PHB disadvantages are stiffness, fragility and low thermal stability and because of this, improvements should be performed. One of the ways to improve these properties is by preparing nanocomposites.

PHB nanocomposites were prepared with the sodium montmorillonite and Cloisite 30B by fusion intercalation. A better compatibility between clay and polymer was established by using Cloisite 30 B and an exfoliated/ intercalated morphology was formed. Moreover, an increase in the crystallization temperature and a decrease in the spherulite size were also observed. The described morphology was responsible for increasing the Young modulus [41]. Besides that, thermal stability was increased in PHB/ organomodified montmorillonite in comparison with pure PHB [42].

5. Polymer/ Clay nanocomposite applications, market and future directons

Approximately 80% of the polymer/ clay nanocomposites is destined to the automotive, aeronautical and packaging industry.

The car part industry pioneered in the use of polymer/ clay nanocomposites, since these nanocomposites present stiffness and thermal and mechanical resistances able to replacemetals, and its use in car reduces powerconsumption. Moreover, its application is possible due to the possibility of being painted together with other car parts, as well as of undergoing the same treatments as metallic materials in vehicle fabrication.

General Motors was the first industry to use nanocomposites in car, reducing its mass byalmost one kilogram. In the past, car parts weremade of polypropylene and glass fillers, which hadthe disharmony with the other car partsas a disadvantage. By using lower filler content, as in the case of the nanocomposites, materials with a higher quality are obtained, as is the case of the nanoSeal™, which can be used in friezes, footboards, station wagon floors and dashboards. Basell, Blackhawk, Automotive Plastics, General Motors, Gitto Global produced polyolefines nanocomposites with, for example polyethylene and polypropylene, to be used in footboards of the Safari and Astro vehicles produced by General Motors.

Car parts, such as handles, rear view mirror, timing belt, components of the gas tank, engine cover, bumper, etc. also used nanocomposites, specially with nylon (polyamide), produced by the companies Bayer, Honeywell Polymer, RTP Company, Toyota Motors, UBE and Unitika.

In the packaging industry, the superior oxygen and dioxide carbon barrier properties of the nylon nanocomposites have been used to produce PET multilayer bottles and films for food and beverage packaging.

In Europe and USA, nanocomposites are used in soft drink and alcoholic beverage bottles and meat and cheese packaging since these materials present an increase in packaging flexibility and tear resistance as well as a humidity control.

Nanocor produced Imperm, a nylon MDXD6/ clay nanocomposite used as a barrier in beer and carbonated drink bottles, in meat and cheese packaging and in internal coating of juice and milk byproduct packaging. The addition of 5% of Imperm in PET bottles increase the shelf time bysix months and reduce the dioxide carbon lossto less than 10%.

Another commercial products can be cited, as for example the M9™, produced by the Mitsubish Gas Chemical Company, for application in juice and beer bottles and multilayer films; Durethan KU2-2601, a polyamide 6 nanocomposite produced by Bayer for coating juice bottles as barrier films and AEGIS™ NC which is polyamide 6/ polyamide nanocomposites, used as barrier in bottles and films, produced by Honeywell Polymer.

In the energy industry, the polymer nanocomposites positively affect the creation of forms of sustainable energy by offering new methods of energy extraction from benign and low-cost resources. One example is the fuel cell membranes; other applications include solar panels, nuclear reactors and capacitors.

In the biomedical industry, the flexibility of the nanocomposites is favorable, which allows their use in a wide range of biomedical applications as they fill several necessary premises for application in medical materials such as biocompatibility, biodegradability and mechanical properties. For this reason and forthe fact of being finely modulated by adding different clay contents, they can be applied in tissue engineering – the hydrogel form, in bone replacement and repair, in dental applications and in medicine control release.

Moreover, there is the starch/ PVA nanocomposite, produced by Novamont AS (Novara, Italy) that can replace the low density PE films to be used as water-soluble washing bags due to its good mechanical properties.

Other commercial applications include cables due to the slow burning and low released heat rate; the replacementof PE tubes withpolyamide 12 nanocomposites (commercial name SET™), produced by Foster Corporation and in furniture and domestic appliances withthe nanocomposite with brand name Forte™ produced by Noble Polymer.

Table 1 presents a summary of the application areas and products in which polymer/ clay nanocomposites are used.

The consumption of polymer/ clay nanocomposites was equal to 90 million dollars with a consumption of 11,300 ton in 2005. In 2011, a consumption of 71,200 ton was expected,corresponding to 393 million dollars.

The scenario that correspond to the areas in which polymer/ clay nanocomposite was used in 2005 is presented in Figure 5. By the end of 2011, the barrier applications were expected to exceed the percentage related to car parts.

In a near future, the PP nanocomposites produced by Bayer are expected to replace car parts that use pure PP and the PC nanocomposites produced by Exaltec are expected to be used in car glasses due to an improved abrasion resistance without loss of optical transparency.

Automotive	Packaging	Energy	Biomedical	Construction	Home furnishings
-footboards, -friezes, - station wagon floors, - dashboards, -timing belts, -handle, -gas tank components, -engine covers, - bumpers.	- beer and soft drink bottles, -meat and cheese packaging, -internal films of juice boxes,	-fuel cells, -lithium batteries, - solar panels - nuclear reactors, -capacitors.	-artificial tissues; -dental and bone prosthesis, -medicines.	-tubes, - cords.	-furniture, -home appliances.

Table 1. Application areas and products that use polymer/ clay nanocomposites.

The research about the application of these nanocomposites in car parts is still being developed since a reduction in the final car mass corresponds to benefits to the environment. The large use of nanocomposites would reduce 1.5 billion liters of gasoline a year and the CO$_2$ emission in more than 5 billion kilograms.

Another thriving field is the barrier applications, the use of which can increase food shelf life besides maintaining film transparency. As an example, by using Imperm nanocomposite in a Pet bottle, beer shelf life is increased to 28.5 weeks.

Great attention has been also paid to the biodegradable polymers which present a variety of applications. Moreover, another potential application is in nanopigment as an alternative to cadmium and palladium pigments which presenthigh toxicity.

The distant future of the applications of polymer/ clay nanocomposites is dependent on the results obtained from researches, commercial sectors, existing markets and the improvement level of the nanocomposite properties. Furthermore, the relevance of their application in large scale, the capital to be invested, production costs and the profits should be taken into account.

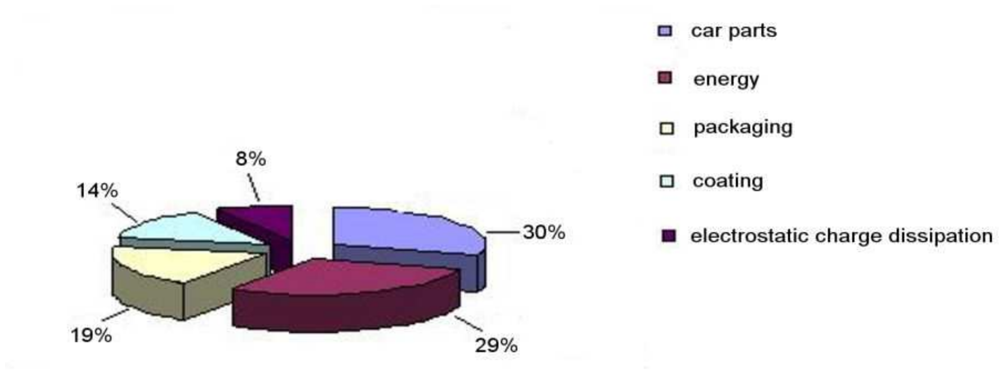


Figure 5. Applications of polymer/ clay nanocomposites in 2005.

Due to the aforementioned reasons, a considerable increase in investigations and the commercialization of nanocomposites in the packaging area, selective catalyzers, conductive polymers and filtration of toxic materials are expected. A light growth in the applications related to an increase of catalysis efficient and of material conductivity, new types of energy, storage information and improved membranes are also expected.

Although nanocomposites present a series of advanced properties, their production is still considered low in comparison with other materials due to the production costs. Once they become cheaper, polymer/ clay nanocomposites can be largely used in a series of applications [11, 43-45].

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