Chapter 1

Conducting Polymers / Layered Double Hydroxides Intercalated Nanocomposites

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Additional information is available at the end of the chapter

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1. Introduction

Layered nanocomposites represent a special class of multifunctional materials that has received a lot of attention over the last years [1-6]. The specific architecture of these composites promotes a synergistic effect between the organic and inorganic parts, generating compounds with different chemical or physical properties as compared with the isolated components. These composites not only represent a creative alternative to the search for new materials, but also allow the development of innovative industrial applications. The potential uses of layered nanocomposites include intelligent membranes and separation devices, photovoltaic devices, fuel cell components, new catalysts, photocatalysts, chemical and biochemical sensors, smart microelectronic devices, micro-optic devices, new cosmetics, sustained release of active molecules, and special materials combining ceramics and polymers, among others [7-18].

A great variety of layered nanocomposites can be prepared from the combination between polymers and layered inorganic solids [1-3]. Compared with the unmodified polymers, the resulting materials present dramatic improvement in properties such as rigidity, chemical and mechanical resistance, density, impermeability to gases, thermal stability, and electrical and thermal conductivity, as well as high degree of optical transparency.

The first successful development concerning the combination of layered inorganic solids with polymers was achieved by researchers from Toyota®, who aimed at structural applications of the nanocomposites in vehicles. These researches prepared nanocomposites by combining nylon-6 and montmorillonite (clay) using the *in situ* polymerization method [20-22]. Research conducted over the past 10 years has shown that nanocomposites containing only a small amount of inorganic silicate (2% volume), exhibit twofold larger elastic modulus and strength

without sacrificing resistance to impact. Other automobile companies began to employ this type of material in their vehicles and intensified research in this area [1-3,21].

The excellent gas barrier and vapor transmission properties of these hybrid nanocomposites have led to their application mainly in food industry, more specifically in food and drink packaging. Incorporation of layered silicate nanoparticles into polymeric matrices creates a labyrinth within the structure, which physically retards the passage of gas molecules [22]. These materials can also be used to coat storage tanks in ships and lines of cryogenic fuels in aerospace systems. Compared with the unmodified polymer, nanocomposites delay fire propagation and enhance thermal stability. In contrast to the amount of additives used in traditional fireproof polymers (60%), these nanocomposites contain low layered inorganic solid loading, typically 2-5 wt%. This is due to the formation of an insulating surface layer that not only slows degradation of the polymer, but also decreases its calorific capacity [1,2]. The decomposition temperature of these nanocomposites can be increased to 100 °C, which extends the use of these materials at ambient temperatures, as in the case of automobile engines.

With respect to environmental applications, layered inorganic solids combined with biodegradable polymers have been employed as reinforcing agents. These materials, called "green" nanocomposites, are an attractive alternative for the replacement of petroleum derivatives in the production of plastics.

Depending on the nature of the components and on the preparation method, two main types of nanocomposites can be obtained from the association of layered compound with polymers, as shown in Figure 1:

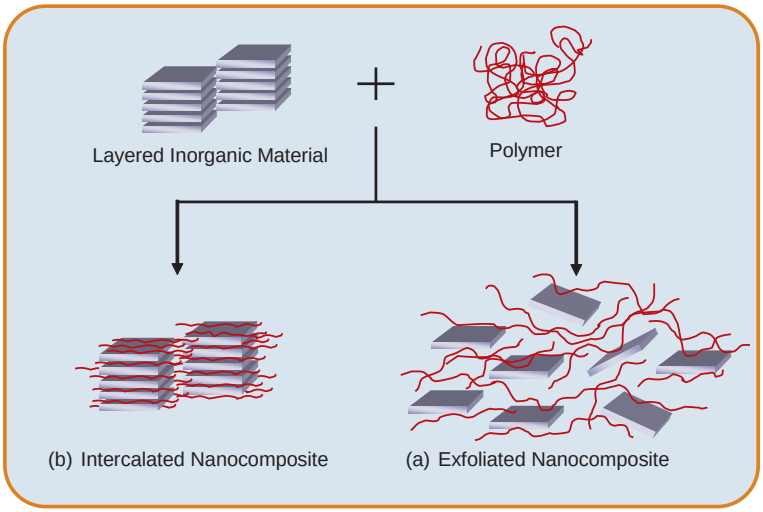


Figure 1. Schematic representation of the different types of composites produced from the interaction between layered compounds and polymers: (a) Intercalated Nanocomposite; (b) Exfoliated Nanocomposite.

- Intercalated Nanocomposite: The polymer is intercalated between the inorganic layers, producing a nanocomposite consisting of polymeric chains and alternating inorganic layers. Intercalation of the polymer often results in increased interlayer spacing; *i.e*, larger distance between two adjacent inorganic layers. (Figure 1a).
- Exfoliated Nanocomposite: The material presents no ordering along the stacking axis of the layer, or the spacing between the inorganic layers is greater than 8 nm. (Figure 1b).
- In addition to the well-defined structures cited above, a third intermediate type of structure can be found, in which the material presents characteristics of intercalation and exfoliation. In this case, there is broadening of the X ray diffraction peaks.
- Several strategies have been utilized for the preparation of organic-inorganic hybrid materials containing layered inorganic solids and polymer [1,2]:
- Exfoliation-adsorption: The layered compound is exfoliated using a solvent in which the polymer is soluble. In some layered compounds there are weak interaction forces between the layers, which can thus be easily exfoliated in appropriate solvents. The polymer may then adsorb onto the exfoliated layers which, after evaporation of the solvent, can be stacked again. As a result, the polymer is intercalated, and an ordered multilayer structure is obtained.
- *In situ* intercalative polymerization: The layered compound undergoes swelling (interlayer expansion) in a solution containing the monomer. The polymer is formed in the interlayer region. The polymerization reaction can be performed by heat or radiation treatment, using an organic initiator or a fixed catalyst.
- Melted polymer intercalation: The layered compound is mixed with the polymer matrix in the melting phase. If the layered surfaces are sufficiently compatible with the selected organic polymer under these conditions, the latter penetrates into the interlayer space, generating an intercalated or exfoliated nanocomposite. This technique does not require any solvent.
- Template Synthesis: This method can only be used for water-soluble polymers. The layered compound is formed *in situ* in an aqueous solution containing the target polymer on the basis of self-assembly forces, the polymer aids nucleation and growth of inorganic layers. As a result, the polymers are retained between the layers.

Among the inorganic solids used in the preparation of layered nanocomposites, one promising class of material is the Layered Double Hydroxides (LDHs), which have been added to polymers for the synthesis of LDH/polymers nanocomposites [23-26]. LDHs can be structurally described as the stacking of positively charged layers intercalated with hydrated anions [27]. In order to better understand the structure of the LDH, it is appropriate to start from the structure of brucite. In this $Mg(OH)_2$ structure, the magnesium cations are located in the center of octahedra, with hydroxyl groups positioned at their vertices. These octahedra share edges, forming neutral planar layers that are held together by hydrogen bonds. In this type of structure, the isomorphic replacement of bivalent cations with trivalent ones creates a positive residual charge in the layers. For charge balance to be reached in the system, anions should be

present between the layers. Together with water molecules, the anions promote stacking of the layers, which culminates in the layered double hydroxide structure displaying a poorly ordered interlayer domain. Not only hydrogen bonding but also electrostatic attraction between the positively charged layers and the interlayer anions hold the layers together in LDHs. A schematic representation of the LDH structure is given in Figure 2.

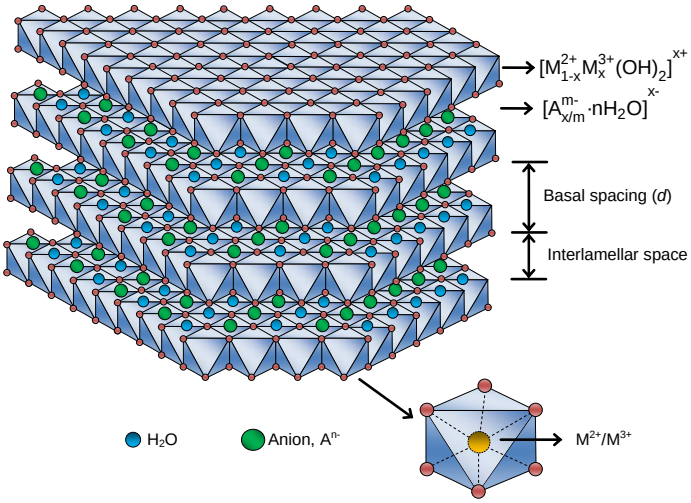


Figure 2. Schematic representation of the LDH structure.

The inorganic layers of the LDH can be stacked according to two different symmetries, resulting in rhombohedral or hexagonal unit cells of the hexagonal system. Most of the synthetic LDH belong to the hexagonal system. Only LDH with M(II)/M(III) ratio equal to 1 are orthorhombic. For the rhombohedral unit cell, the parameter c is three times the basal spacing, space group R3m. In the case of the hexagonal unit cell, the parameter *c* is twice the basal spacing, space group P63mmc. The notations 3R and 2H refer to unit cells as rhombohedral or hexagonal, respectively.

In the structure of LDH, the interlayer domain comprises the region between adjacent inorganic layers. This region is composed of randomly distributed anions and water molecules. Powder X ray diffraction (PXRD) and EXAFS studies, performed by Rousselet et al. showed the highly disordered nature of this region [28]. Besides being found in the interlayer domain, where they hydrate the intercalated anions, the water molecules can also be adsorbed between the crystallites. The water molecules onto the surface of the micro crystallites surface are called extrinsic water molecules, whereas those that are located in the interlayer domain are designated intrinsic water molecules. The global hydration status of the LDH is the addition of both terms, intrinsic hydration and extrinsic hydration. Many researchers consider the interlayer domain of LDH a quasi-liquid state, which gives high mobility to the interlayer anions.

A wide variety of anions can be intercalated into the LDH; for example, organic anions, inorganics and organic-inorganics, and polymers. The intercalation of more than one type of anion in the interlayer domain is an extremely rare phenomenon. Usually, the presence of two or more kinds of anions during the synthesis generates a competition between these anions, and the one with greater tendency to stabilize the system and/or that is present in larger amount will be intercalated. Using PXRD and *in situ* X ray energy dispersion spectroscopy techniques, Fogg et al. reported the existence of a second intermediate stage due to co-intercalation of Cl^- ions and succinate in LiAl-LDH [29]. Pisson et al. studied the exchange of Cl^- anions with succinate and tartarate anions in LDH of the system [Zn_2Al-Cl], [Zn_2Cr-Cl], and [Cu_2Cr-Cl]. The exchange reaction was monitored *in situ* by the X ray diffraction and X ray energy dispersion spectroscopy techniques. The analyses revealed the formation of a second intermediate stage in all the materials, caused by co-intercalation of organic anions and chloride ions [30]. Kaneyoshi and Jones demonstrated that terephthalate anions can adopt two different orientations in relation to the inorganic layers when they are intercalated into Mg-Al-LDH. The longer molecular axis is either perpendicular or parallel to the plane of the layers. These two orientations are known as interstratified intermediated phases. The occurrence of these two orientations of intercalated terephthalate anions was supported by the appearance of a third basal spacing, attributed to the contribution of two different orientations of anions in the interlayer domain.

A large number of natural and synthetic LDHs containing various metal cations have been studied. In order to form the LDH, the metal cations that will be part of the inorganic layer must present octahedral coordination and ion radius in the range of 0.50 to 0.74 Å. By varying the metal cations, the proportion among them, and the interlayer anion, a large variety of LDH can be prepared. Countless cations can be part of this structure: Mg^{2+}, Al^{3+}, most of the cations of the first transition period, Cd^{2+}, Ga^{3+}, and La^{3+}, among others [27]. In addition LDH displaying more than one bivalent and/or trivalent cation can be synthesized, which further expands the compositional possibilities.

The ratio between the metal cations M(II)/M(III) is also very important, because a change in this ratio between modifies the charge density in the layers, since the charge is generated from the isomorphic substitution of bivalent cations with trivalent ones in the structure of the inorganic layers [27,32]. There is controversy over the values that the x parameter in the general formula of the LDH can assume during the synthesis of these materials. According to de Roy et al., the x value should lie between 0.14 and 0.50, for the formation of an LDH where the M(II)/M(III) ratio can vary between 1 and 6 [33]. For Cavani et al., the x value must fall between 0.20 and 0.34, with the M(II)/M(III) ratio ranging between 2 and 4.37. However, some researchers have reported the synthesis of LDH with different M(II) to M(III) ratios from those mentioned above [27].

As described earlier, the interlayer domain consists of water molecules and anions, mainly. Practically, there is no limitation to the nature of anions that can compensate the residual positive charge of the LDH layers. However, obtaining pure and crystalline materials is not an easy task. Generally, simple inorganic anions with higher charge/radius ratio have greater tendency for intercalation. This is because these anions interact more strongly with the inorganic layers from an electrostatic viewpoint. For the intercalation of organic anions, especially anionic poly-

mers, factors such as the size and geometry of the anion, the interaction between them, and the ratio between size and charge must be taken into account. Some interlayer anions are more mobile, which gives the resulting materials good exchange properties.

Several factors must be borne in mind when planning the synthesis of LDH. For instance, the degree of substitution of M(II) with M(III) cations, the nature of the cation, the nature of the interlayer anion, the pH of the synthesis and, in some cases, the controlled atmosphere. Furthermore, to obtain materials with good crystallinity, the concentrations of the solutions, the rate of the addition of the solutions, the stirring rate, the final pH of the suspension (for variable pH methods), the pH during the addition (for constant pH method), and the temperature of the mixture (typically performed at room temperature) must be controlled. There are a number of methods that can be used for the synthesis of LDH. They can be divided into two categories:

i. Direct synthesis methods: salt-base method or co-precipitation (at variable pH or at constant pH), salt-oxide method, hydrothermal synthesis, induced hydrolysis, sol-gel method, and electrochemical preparation [27,33-37].

ii. Indirect synthesis methods: simple anionic exchange method, anionic exchange by regeneration of the calcined material, and anion exchange using double phase, with formation of a salt between the surfactants [33,38,39].

Among the most extensively investigated conducting polymers are polyacetylene; polyheterocyclic five-membered compounds like polypyrrole, polythiophene, and polyfuran; and polyaromatics such as polyaniline and poly (p-phenylene).The structures and respective electrical conductivity values of some conductive polymers are summarized in Table 1 [40].

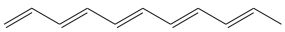
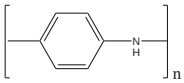
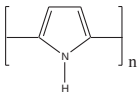
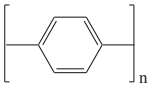
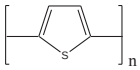
Name	Structural Formula	Conductivity / $S \cdot cm^{-1}$
Polyacetylene		10^3 a 10^6
Polyaniline		10 a 10^3
Polypyrrole		600
Poly(*p*-phenylene)		500
Polythiophene		200

Table 1. Structure and electrical conductivity values of some conductive polymers [40].

Below, we will outline some classes of conducting polymers:

a. Polyaniline:

Polyanilines are widely studied because of their low cost, good stability in the presence of oxygen and water, and interesting redox properties. In 1835, polyaniline was first synthesized as "black aniline", a term used for the product obtained by oxidation of aniline [41]. Some years later, Fritzche analyzed the products obtained by chemical oxidation of this aromatic amine [42]. In 1862, Letheby found that the anodic oxidation of aniline in a platinum electrode, in an aqueous solution of sulfuric acid, formed a dark brown precipitate [43]. The polyaniline chain consists of units present in two main forms: (i) the fully reduced form, which contains only aromatic rings and nitrogen atoms of the amine function, shown in Figure 3a, and (ii) a completely oxidized form displaying iminic nitrogen atoms, quinonics rings, and aromatic rings, as represented in Figure 3b.

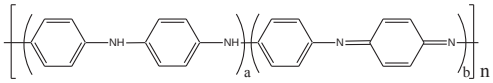
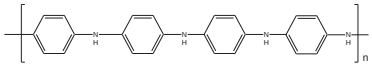
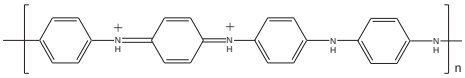
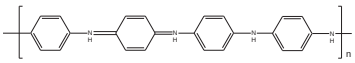
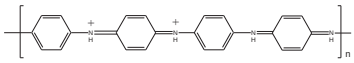


Figure 3. Representation of the general structure of the polyaniline base form: (a) reduced species (b) oxidized species.

Gospodinova and Terlemezyan examined the oxidation state of polyaniline constituents. The principal oxidation states of polyaniline are presented in Table 2 [44]. The emeraldine salt is the structural form of polyaniline that affords higher conductivity values. Polyaniline can be doped by protonation, with no change in the number of electrons in the polymer chain.

Oxidation state	Strucuture	Color	Characteristic
Leucoemeraldine		Yellow 310	Insulating, completely reduced
Emeraldine salt		Green 320, 420, 800	Conductive, half-oxidized
Emeraldine base		Blue 320, 620	Insulating, half-oxidized
Pernigraniline		Purple 320, 530	Insulating, completely oxidized

* The numerical values refer to the wavelength (in nanometers) where absorption is maximum.

Table 2. Most important oxidation states of polyaniline [44].*

b. Polypyrrole:

The first report about pyrrole was published by Runge in 1834. This author observed a red component in coal tar and bone oil. The compound isolated and purified from this component was named of pyrrole [45]. The structural formula of pyrrole was established in 1870. In the late 19th century, the interest in pyrrole and its derivatives was aroused, following the discovery that this molecule was part of some porphyrins found in biological systems, such as chlorophyll. Approximately 100 years after the first report on the discovery of pyrrole, *i.e*, in 1970, interest in these materials increased again due to the possibility of preparing conducting polypyrroles [46].

Pyrrole is a five-membered cyclic compound (heterocyclic) containing 6 π electrons. Additionally, pyrrole has an sp^2 nitrogen, and its three σ bonds are located in the plane of the ring. The excess electron, the conjugation of the double bonds, and their ability to relocate are the structural characteristics underlying the charge conduction properties presented by the pyrrole polymer products.

c. Polythiophene:

In 1882, Meyer discovered thiophene [47]. At that time, his studies revealed that this compound, which was isolated from benzene impurities, was a new aromatic system. Thiophene is not a component of animal metabolism, but some thiophene derivatives can be found in plants. Thiophene derivatives are widely employed in many types of chemical industry, including the pharmaceutical, veterinary, polymers, and agrochemicals industries.

Thiophene is a compound analogous to pyrrole. Instead of the nitrogen heteroatom, it contains a sulfur atom with sp^2 hybridization. The sp^2 orbital, which is perpendicular to the π electron system, has an unshared electron pair. The p-orbital of sulfur donates two electrons to the π system. Polythiophene derivatives have been extensively studied, probably because most of them are soluble in organic solvents, which facilitates processing of the material.

The electrical conductivity of a solid is the result of the number of charge carriers (electrons / holes) and their mobility. Conducting polymers have a large number of charge carriers with low mobility, which is mainly caused by the large number of structural defects such as reticulation and the disordering of chains. The formation of nanocomposites by intercalation of conductive polymers into LDH can minimize the formation of reticulation defects and the disordering of polymer chains, furnishing materials with new and interesting properties. Table 3 summarizes the literature works on the synthesis and characterization of conducting polymers intercalated into LDH.

Year	Nanocomposites	Examples	Authors	Ref.
1994	LDH / polyaniline	CuCr- polyaniline-LDH CuAl- polyaniline-LDH	Challier and Slade	48
2001	LDH / aminobenzoate derivatives	LiAl-*o*-, *p*- and *m*-aminobenzoate-LDHs	Isupov et al.	49

2002	LDH / aniline sulfonate	CuCr- aniline sulfonate-LDH	Moujahid et al.	50
2003	LDH / aminobenzene sulfonate	CuCr- aminobenzene sulfonate-LDH	Moujahid et al.	51
2004	LDH / 2-thiophenecarboxylate	ZnAl-2-thiophenecarboxylate-LDH ZnCr-2-thiophenecarboxylate-LDH	Tronto et al.	52
2005	LDH / aniline sulfonate derivatives	CuCr-*o*- and *m*-aminobenzenesulfonate, 3-amino-4-methoxybenzenesulfonate, 3-aniline-1-propane sulfonate, and 4-aniline-1-butane sulfonate-LDHs.	Moujahid et al.	53
2006	LDH / pyrrol derivatives	ZnAl-4-(1H-pyrrol-1-yl)benzoate-LDH ZnCr-4-(1H-pyrrol-1-yl)benzoate-LDH ZnAl-3-(pyrrol-1-yl)-propanoate-LDH ZnAl-7-(pyrrol-1-yl)-heptanoate-LDH	Tronto et al.	54 55 56
2006	LDH / aminobenzoate derivatives	MgAl-aminobenzoate-LDH NiAl-aminobenzoate-LDH	Tian et al.	57 58
2006	LDH / aniline sulfonic	NiAl-aniline sulfonic -LDH	Wei et al.	59

Table 3. Some examples of Nanocomposites consisting of LDH/conductive polymers.

Challier and Slade reported the synthesis and characterization of layered nanocomposites of CuCr and CuAl-LDHs intercalated with polyaniline [48]. The oxidizing host matrices were prepared by the coprecipitation method, with the intercalation of terephthalate anions into CuCr-LDH and hexacyanoferrate(II) anions into CuAl-LDH. Then, the LDH precursors were submitted to an anion exchange reaction with a solution of pure aniline under reflux, for 24 h. The X ray diffractograms showed that the materials submitted to reaction with aniline exhibited basal spacings of 13.3 Å and 13.5 Å for CuCr-LDH and CuAl-LDH, respectively. This result was consistent with the intercalation of aniline molecules containing aromatic rings oriented perpendicular to the plane of the layers. FTIR analyses evidenced polymerization of the aniline molecules, since the absorption spectra displayed bands typical of the emeraldine form. According to the authors, the oxidant character of Cu^{2+}, present in layered structure of the inorganic host, helped induce oxidative polymerization of the aniline intercalated in the interlayer galleries.

Isupov et al. described the intercalation of *o*-, *p*-, and *m*-aminobenzoate anions into LiAl-LDH [49]. The incorporation of aminobenzoate anions in the host matrices was conducted by anion exchange, from an LiAl-LDH intercalated with chloride anions. The basal spacings obtained from the X ray diffractograms indicated that the anion exchange reaction was effective, with incorporation of aminobenzoate anions in the interlayer domain. To carry out the *in situ* polymerization, samples of the nanocomposites were submitted to a heat-treatment at 90 °C for 100 h, with 75% relative air humidity. For the LiAl-LDH intercalated with *m*-aminobenzoate anions, the formation of a polyconjugated system was confirmed by ESR spectra performed in vacuum at 77 K and 300 K. The spectra displayed a broad isotropic signal between 7.3 and 7.5 G, with g = 2.000 and line with Gaussian shape. Heating of the nanocomposite in air

intensified the ESR signal. Formation of the polyconjugated system was also corroborated by FTIR and Raman spectroscopies. A comparison of the FTIR spectrum of LiAl-LDH intercalated with *m*-aminobenzoate and its oxidation products revealed a marked decrease in the band located at 1250 cm^{-1}, which indicates a decrease in the number of amino groups, $-NH_2$.

Moujahid et al. reported the intercalation of the *m*- and *o*-aminebenzeno sulfonate anion, 3-amine-4-methoxybenzene sulfonate, 3-aniline-1-propane sulfonate and 4-aniline-1-butane sulfonate into Cu_2Cr-LDHs [50,51,53]. These authors discussed the arrangement of intercalated molecules and their subsequent dimerization and/or *in situ* polymerization. The authors incorporated these inorganic anions between the layers was by the direct precipitation method at constant pH. After the synthesis, the resulting materials were submitted to heat treatment at different temperatures, under air atmosphere. The interlayer distances of they synthesize nanocomposites were consistent with the presence of a bilayer of guest molecules in the interlayer space. The heat treatment performed at 350 K culminated in a contraction in the basal spacing of the nanocomposites, except for the material intercalated with the *o*-amine-benzene sulfonate anions. This contraction was associated with reorientation of the intercalated molecules and/or with an *in situ* polymerization. At temperatures above 350 K up to approximately 450 K, there was no significant variation in basal spacing. ESR analysis evidenced *in situ* polymerization. The profiles of the ESR spectra changed with increasing temperature. The value of the signal g (g = 2.0034 ± 0.0004) was typical of the formation of organic radicals and/or conduction electron. For the nanocomposite intercalated with the *m*-aminobenzene sulfonate anion, the ESR and CV analysis showed that the *in situ* polymerization must occur with a syndiotactic arrangement. For the nanocomposite intercalated with the *o*-aminobenzene sulfonate anion, the ESR studies indicated a very weak response of spin carriers for these materials. The electrochemical characterization did not show the presence of reversible redox processes. These results, together with the constancy of the basal spacing value obtained up to a temperature of 450 K, suggested that *in situ* polymerization was not favored when the monomer had the amino group located at the *ortho* position relative to the sulfonate group. For the 3-amine-4-methoxybenzene sulfonate anion, the presence of methoxy group in the *para* position relative to the sulfonate group made the polymerization process difficult. The ESR and CV data for this nanocomposite indicated formation of a dimer. For the nanocomposites synthesized with 3-aniline-1-propane sulfonate and 4-aniline-1-butane sulfonate, the heat-treatment at 473 K prompted an increase in g (g = 2.0034 ± 0.0004), which is associated with the generation of organic radicals and/or conduction electrons.

Tronto et al. described the synthesis, characterization, and electrochemical investigation of 2-thiophenecarboxylate intercalated into ZnAl-LDH and ZnCr-LDH [52]. The materials were synthesized by the coprecipitation method at constant pH, followed by hydrothermal treatment at 65 ^{o}C for 72 h. The LDH were analyzed by PXRD, FT-IR, ^{13}C CP-MAS, TEM and CV. The basal spacing was about 15.3 Å for all the LDH which suggested the formation of bilayers of anions intercalated between the inorganic sheets. In this configuration, the 2-thiophenecarboxylate anions would be in a position in which their longer axes would lie perpendicular to the plane of the inorganic layers. Besides the phase with basal spacing of 15.3 Å, another phase with basal spacing of 7.58 Å was also detected in the diffractograms. This value was similar to

some values reported for the intercalation of CO_3^{2-} anions into ZnAl-LDH and ZnCr-LDH. However, the qualitative analysis and ^{13}C CP-MAS did not confirm the presence of carbonate anions, as contaminant in the LDH. Thus, the results indicated that for this second phase, 2-thiophenecarboxylate anions were intercalated with their longer axes parallel to the plane of the inorganic layer. ^{13}C CP-MAS data further suggested that, during the synthesis, the 2-thiophenecarboxylate anions lost an acid hydrogen which led to formation of the dimer.

Tronto et al. conducted a study on the *in situ* polymerization of pyrrole derivatives, 4-(1H-pyrrol-1-yl)benzoate, 3-(Pyrrol-1-yl)-propanoate, and 7-(pyrrol-1-yl)-heptanoate, intercalated into LDH [54-56]. The materials were synthesized by co-precipitation at constant pH, followed of hydrothermal treatment for 72 h. The final LDH were characterized by X ray diffraction, ^{13}C CP-MAS NMR, TGA, and ESR. The basal spacing value coincided with the formation of bilayers of intercalated monomers. ^{13}C CP-MAS NMR and ESR analyses showed the formation of a polyconjugated system with polymerization of the monomers intercalated in the LDH during the coprecipitation and/or hydrothermal treatment processes. This result reinforced the authors assumption that the connectivity between the monomers occurred spontaneously during the synthesis, with generation of oligomers and/or syndiotactic polymers intercalated between the LDH layers. At room temperature, the ESR spectrum displayed a signal typical of the hyperfine structure (hfs). The presence of hfs suggested the existence of a proper regulatory environment for the free electrons. These electrons would be present in an organic "backbone" of small size. Thermal analysis of these materials revealed that the inorganic host matrix provided the intercalated polymers with thermal protection, because the thermal decomposition reactions happened at higher temperatures compared with the pure polymers.

Tian and cols. investigated the oxidative polymerization of *m*-$NH_2C_6H_4SO_3^-$ anions intercalated into NiAl-LDH using ammonium persulfate as the oxidizing agent [57]. The amount of oxidizing agent required for controlled polymerization of the intercalated monomers was systematically evaluated. The materials were characterized by PXRD, UV-Vis spectroscopy, FT-IR spectroscopy, and XPS determination. PXRD and elemental analysis data showed the co-intercalation of nitrate anions, originating from the LDH precursor, and *m*-$NH_2C_6H_4SO_3^-$ anions. UV-Vis results evidenced polymerization of the intercalated *m*-$NH_2C_6H_4SO_3^-$ anions, with the formation of small chains. The intercalated polyaniline sulfonate was present in different oxidation states and at different protonation levels, depending upon the amount of oxidizing agent that was added.

Tian and cols. also performed the *in situ* oxidative polymerization of *m*-$NH_2C_6H_4SO_3^-$ anions intercalated into MgAl-LDH [58]. The monomers were incorporated into the LDH via an exchange reaction using the precursor $[MgAl(OH)_6](NO_3)\ nH_2O$. The nitrate anions remaing from the exchange reaction and co-intercalated with the *m*-$NH_2C_6H_4SO_3^-$ anions were utilized as oxidizing agent for the oxidative polymerization of the intercalated monomers. The resulting materials were analyzed by DTA-TG-DSC as well as UV-Vis and HT-XRD spectroscopies. In the temperature range 300-350 ^oC, the UV-Vis analysis confirmed the reduction of nitrate and polymerization of aniline.

Wei et al. reported the oxidative polymerization of *m*-$NH_2C_6H_4SO_3^-$ anions in NiAl-LDH, using intercalated nitrate anions as the oxidizing agent [59]. The LDH interlayer space was used as

a "nanoreactor" for the *in situ* polymerization of the intercalated monomer. Polymerization of the monomers was acomplished by heat treatment under nitrogen atmosphere. The interlayer polymerization was monitored by thermogravimetric analysis coupled with differential thermal analysis and mass spectrometry (TGA-DTA-MS), UV-Vis spectroscopy, X ray absorption near edge (XANES), (HT-XRD) and FTIR spectroscopy. Polymerization of the monomer was observed at a temperature of 300°C.

2. Synthetic strategies for the preparation of conducting polymers / layered double hydroxides intercalated nanocomposites

The synthesis of intercalated nanocomposites of LDH/conductive polymers can be carried out using different strategies. The main ones are [23]:

1. Intercalation of monomer molecules between the LDH layers, with subsequent *in situ* polymerization. Intercalation of the monomer can occur by direct or indirect methods. The intercalation of monomer molecules with subsequent *in situ* polymerization, is widely used in the preparation of various LDH/conductive polymers. The resulting nanocomposites generally exhibit good structural organization and phase purity. This process is limited by two factors:

- **i.** the distance between the monomers when they are strongly linked, or grafted, to the structure of the inorganic layers. When the monomers are strongly bound to the layers, their flexibility (freedom of movement within the interlayer) is limited, so the proximity between them should be sufficient for the polymerization reaction to occur. High charge densities in the layers may shorten distance between the intercalated monomers. Functionalized monomers with long chain aliphatic groups also provide greater flexibility.
- **ii.** the polymerization conditions (temperature, pH, or redox reaction), which should be selected so as not to affect the layered structure of the resulting materials.

Indirect methods may also be employed for the intercalation of monomers. These methods are often utilized when the chemical nature of the interlayer space and guest species are not compatible. Such methods require the preparation of an LDH precursor intercalated with a molecule that can be easily exchanged. This LDH precursor is then placed in contact with the monomer of interest, which will replace the previously intercalated anion. To obtain the LDH/polymer, it is necessary to carry out the *in situ* polymerization reaction after the exchange with the monomer.

2. Direct intercalation of polymer molecules with low molecular weight between the LDH layers or intercalation polymers with high molecular weight by indirect methods. The incorporation of the polymer between the LDH layers, can be performed by direct method by using the direct co-precipitation reaction, nanocomposites containing polymers that have an anionic group; for example, carboxylate or sulfonate groups, can be produced

during growth of the inorganic crystal. This preparation strategy usually yields nanocomposites with low structural organization. The crystallinity of these materials can be improved by hydrothermal treatment. The indirect method requires the presence of the LDH precursor, usually containing chloride anions. This LDH precursor is placed into exchange reaction using suitable solvents in the presence of the polymer of interest.

3. Intercalation of LDH via exfoliation, when a colloidal system is formed between the LDH and an appropriate solvent, for exfoliation of the layers. Restacking of the layers in the presence of a solution containing the target monomer or polymer culminates in their intercalation by restacking of the structure of the layer. When the monomers are intercalated, a subsequent *in situ* polymerization is required for attainment of the intercalated nanocomposite LDH/polymer. This strategy is usually employed when the polymer has high molecular weight, which makes their diffusion between the LDH layers difficult. Due to its high charge density, the LDH does not have a natural tendency to exfoliation. To achieve delamination of these materials, it is necessary to reduce the electrostatic interaction between the layers. This can be done with intercalation of spacer anions, such as, dodecylsulfonate and dodecylbenzenesulfonate. Exfoliation is then obtained by placing the organically modified LDH in a solution containing a polar solvent. Addition of polymer to the solution containing the exfoliated material results in the formation of an intercalated and/or exfoliated precipitate. In some cases, the nanocomposite is only generated upon evaporation of the solvent.

In addition to the strategies described above, immobilization of the polymer between the LDH inorganic sheets can also be attained by regeneration of the layered structure using the "*memory effect*" exhibited by some LDH. In this case, a previously prepared LDH, normally MgAl-CO_3, is firstly calcined at an adequate temperature, for elimination of the interlayer anion. The calcined material, a mixed oxy-hydroxide, is then placed in contact with an aqueous solution of the polymer to be intercalated. The oxide is hydrolyzed with regeneration of the LDH structure and intercalation of the polymer. This process is accompanied by a sharp increase in the pH value. The latter can be corrected, to prevent the intercalation of hydroxyl anions. Normally, the LDH/polymers nanocomposites produced by this method do not exhibit good organization, being more suitable for the incorporation of small molecules. This method was used for the intercalation of silicates into LDH. In this case, mexinerite (an MgxAlOH-LDH, with x = 2, 3, 4) was employed as precursor for incorporation of the silicate to this end, mexinerite was previously calcined at 500 ^{o}C under air atmosphere, and then placed in contact with a solution of tetraethylorthosilicate, $Si(OC_2H_5)_4$ (TEOS). This afforded more crystalline materials than those obtained by anion exchange or direct co-precipitation, using metasilicate and ZnM-LDHs (M = Al, Cr).

An additional route for preparation of the LDH/polymer is the auxiliary solvent method. Solvents represent an important part in the swelling processes of the layered materials, since they promote separation of the layers. Schematic representation of the incorporation of polymers into layered double hydroxides is given in Figure 4.

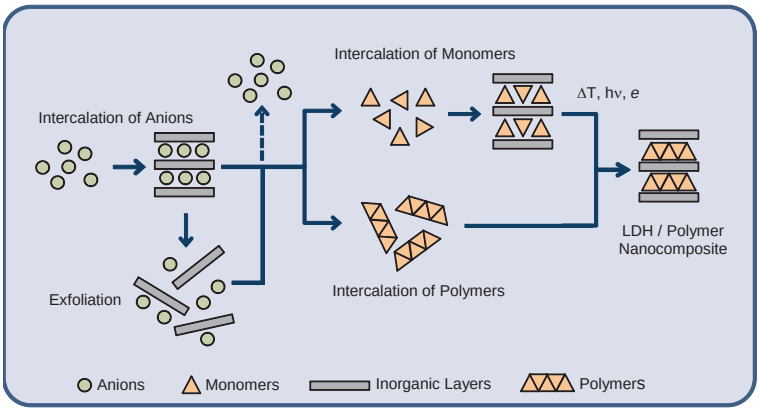


Figure 4. Schematic representation of the incorporation of polymers into layered double hydroxides. *(adapted from ref. 23)*

3. Characterization methods

This section describes the main techniques employed for the characterization of intercalated nanocomposites of conducting polymer / LDH: Powder X-ray Diffraction (PXRD), ^{13}C Cross-Polarization/Magnetic Angle Spinning (CP/MAS) NMR spectroscopy, Electron Spin Resonance (ESR) spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared (FTIR) spectroscopy, Ultraviolet/Visible (UV-Vis) Spectroscopy, Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM).

3.1. Powder X-ray Diffraction (PXRD)

The X ray diffraction pattern (PXRD) of LDH presents basal peaks 00*l* related to the stacking sequence of the inorganic sheet. The peaks are not basal, said to non harmonics, are related to the sheet structure. For new LDHs, the indexing of the diffraction peaks can be accomplished by comparison with the PXRD of hydrotalcite, which exists in the database of diffraction equipment (JCPDS-ICDD, PDF database), or with a number of other LDHs described in the literature. Figure 5 brings a representative PXRD for an MgAl-CO_3-LDH.

The interlayer distances can be calculated from the values of 2θ, using the Bragg equation:

$$n\lambda = 2d_{hkl} \cdot sen\theta$$

where n is the diffraction order, d_{hkl} is the interlayer spacing for the peak hkl, and θ is the Bragg angle, determined by the diffraction peak. Repetition of the d value, for $n = 1, 2, 3...$, evidences the formation of a layered material. The interlayer spacing can be calculated by averaging the basal peaks according to the equation:

http://dx.doi.org/10.5772/54803

$$d=\frac{1}{n}(d_{003}+2d_{006}+...+nd_{00n})$$

The parameters *a* and *c* can be obtained according to the equation:

$$\frac{1}{(d_{hkl})^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}$$

where h, k, and l are the Miller indices of the corresponding peak. For a LDH with stacking sequence 3R, the *c* parameter c is equal to three times the basal spacing value.

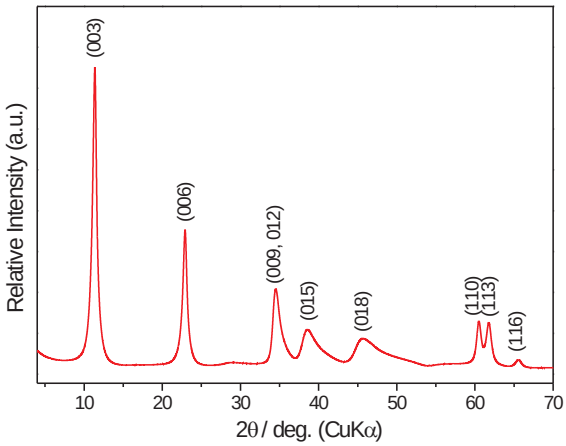


Figure 5. PXRD of synthetic Hydrotalcite.

To determine the orientation adopted by anionic species, such as monomers and polymers intercalated into LDHs, the values of interlayer spacing and/or basal spacing obtained from the PXRD data are compared with the size of anions obtained by specific computer programs, like "VASP (*Vienna Ab-initio Simulation Package*)".

When thermal treatments is performed for the *in situ* polymerization of monomers intercalated between the LDHs inorganic layers, the PXRD analysis may reveal a decrease in the value of interlayer spacing, which indicates a small contraction between adjacent layers. The presence of phases, other than the LDH can also be identified by PXRD, which is useful since thermal treatment may often generated oxides.

3.2. ^{13}C Cross-Polarization/Magnetic Angle Spinning (CP/MAS) NMR spectroscopy

In situ polymerization of monomers intercalated into LDH may be monitored by ^{13}C Cross-Polarization/Magnetic Angle Spinning (CP/MAS) NMR spectroscopy. This technique detects

formation of bonds of the monomer-monomer type in polyconjugated systems. Assignment of the chemical shift values for the monomers can be carried out by computer simulation using specific computer programs, such as "*ACD/ChemSketch, version 4.04*", provided by the company Advanced Chemistry Development Inc., and "*CS Chemdraw Ultra®*", offered by the company Cambridgesoft Corporation. The values obtained by simulation can be compared with the values achieved experimentally.

Figure 6 contains an example of ^{13}C Cross-Polarization/Magnetic Angle Spinning (CP/MAS) NMR Spectroscopy analyses for the *in situ* polymerization of 4-(1H-pyrrol-1-yl)benzoate intercalated into ZnAl-LDH [54]. Assignment of the peaks to the carbons of the monomer is given in Table 4.

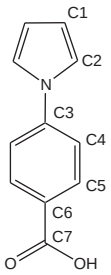
Notation	Assignment (Cn)	DMSO-D6 (ppm)	CP-MAS (75.4 MHz) (ppm)
	C1	111.3	111.2
	C2	118.9	120.1
	C3	143.0	142.3
	C4	118.5	115.6
	C5	130.9	132.9
	C6	127.0	122.8
	C7	166.6	174.9

Table 4. Assignment of the peaks to the carbons in the ^{13}C CP-MAS NMR analyses of 4-(1H-pyrrol-1-yl)benzoate.

The ^{13}C CP/MAS NMR spectra of all LDH were similar. In the Figure 6c and 6d, the peaks can be unambiguously assigned as carbons C7 (175.1 ppm), C5 (131.6 ppm), C3 (140.8 ppm), and C1 (113.7 ppm). The broad signal at 116.8 ppm can be attributed to the chemical shifts of the remaining carbons C4 and C6 of the six-membered ring. Several simulations of the ^{13}C NMR spectra suggest that one possible quaternary carbon, resulting from the polymerization of the monomer via condensation C2-C2, presents chemical shift in the range of 112.0 to 116.0 ppm. Therefore, the large signal at 116.8 ppm in spectrum of the polymer is ascribed to this quaternary carbon, coinciding with the chemical shifts of the remaining carbons C4 and C6. Together with the PXRD results, these data suggest that the production of oligomers and/or polymers occurs with the formation of bilayers of monomers in the interlayer space. In this arrangement, the carboxylate groups are directed to the layer, whereas the aromatic rings occupy the central region of the interlayer spacing. Therefore, the polymer obtained within the interlayer resembles a "*zig-zag*", similar to the polymers of the syndiotactic type.

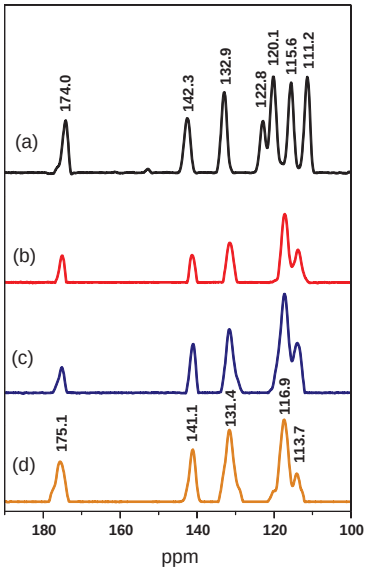


Figure 6. CP-MAS NMR spectra of: (a) pyrrolebenzoic acid; (b) ZnAl-4-(1H-pyrrol-1-yl)benzoate-LDH; (c) ZnAl-4-(1H-pyrrol-1-yl)benzoate-LDH with hydrothermal treatment; and (d) ZnAl-4-(1H-pyrrol-1-yl)benzoate-LDH after thermal treatment [54].

3.3. Electron Spin Resonance (ESR) spectroscopy

Electron Spin Resonance (ESR) spectroscopy allows for monitoring of *in situ* polymerization processes in intercalated monomers. The spectra of conducting polymers usually exhibit signs typical of the formation of polarons, with the Lorentzian profile. In these analyses, the apparatus is normally operated at 9.658 GHz, using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical to determine the ressonance frequency (g = 2.0036 +/- 0.0002). The scan width can vary between 2000 and 4000 G, with a receiver gain of 100000.

Figure 7 illustrates ESR analyses for monitoring of the *in situ* polymerization of 3-(Pyrrol-1-yl)-propanoate monomers intercalated into ZnAl-LDH [55,56]. The spectra were recorded after heat-treatment at temperatures ranging from ambient to 180 °C for 2h. For material at room temperature, the ESR spectra display very weak signals. Thus, the spectrum was enlarged 16 times for comparison with those of the material treated at other temperatures. Typical signs can be noticed for the "*superhyperfine*" structure with 6 lines, and there is a sign characteristic of the formation of a polaron with g = 2.004 ± 0.0004. The appearance of this "*superhyperfine*" structure suggest formation of the radical (COO·). The magnetic moment of this radical should interact with the magnetic moments of the nuclei of the aluminum atoms present in the inorganic host matrix. This hypothesis considers the nuclear spin of aluminum as I = 5/2 and a number of nuclei N = 1, which generates a spectrum of 2NI + 1 = 6 lines. Due to the charge

balance required for maintenance of the electroneutrality of hybrid systems there a regulating environment for the free electrons of the radicals (COO ·) within the interlayer spacing. These radicals are located near the aluminum cations, because the latter are responsible for the positive charge density of the layer. The signal at g = 2.004 ± 0.0004 attests to the formation of a polaron, *i.e.*, a polarized entity resulting from delocalization of the radical in structures with π conjugations. The increase in the delocalization of π orbitals favors the generation of polarons, so an increase signal in this upon heat-treatment indicates stronger connection between the monomers. The Lorentzian profile of the ESR spectrum of the material at room temperature is compatible with the formation of conjugated polymers. The ESR results agree with the NMR results and indicate that spontaneous partial polymerization and/or oligomerization of the 3-(Pyrrol-1-yl)-propanoate monomers takes place during coprecipitation of the nanocomposites.

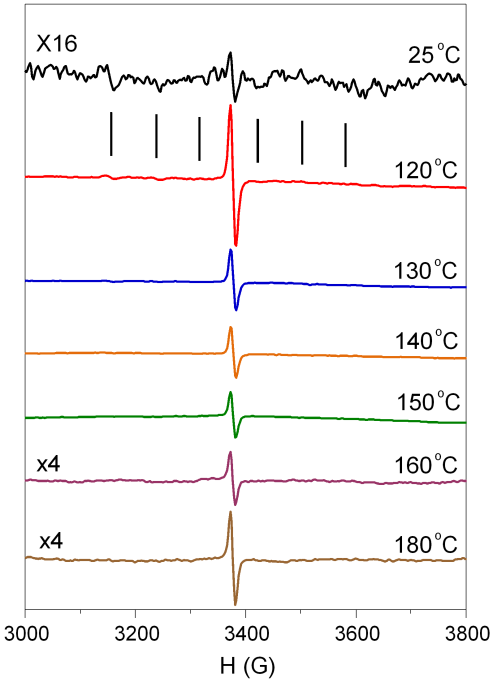


Figure 7. ESR spectra of Zn-Al-3-(Pyrrol-1-yl)-propanoate-LDH as a function of the heat-treatment temperature [55,56].

3.4. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The thermal stability of LDHs intercalated with conductive polymers as well as the amount of water, intercalated and adsorbed, in the nanocomposites can be determined by thermogravimetric analysis. The results are obtained as a curve mass decrease (%) *versus* temperature. For

the LDHs, the thermal decomposition steps generally overlap, especially in the case of LDHs intercalated with organic molecules.

TGA is important in the thermal *in situ* polymerization of nanocomposites, since it is necessary to determine the temperature that should be used for polymerization of the intercalated monomers. The thermal decomposition of intercalated organic compounds takes place at higher temperatures, so it is possible to achieve greater thermal stability for conducting polymers intercalated into an inorganic host matrix (LDH).

Figure 8 displays an example of TGA/DSC analysis for the ZnAl-LDH intercalated with 3-aminobenzoate monomers and for the pure monomer.

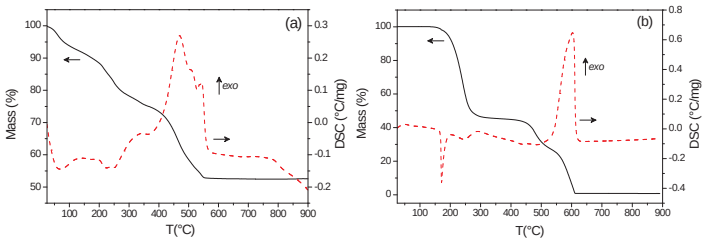


Figure 8. TGA-DSC of (a) ZnAl-3-aminobenzoate-LDH; (b) sodium 3-aminobenzoate [60].

For the nanocomposite material, Figure 8a, the early stages of thermal decomposition are associated with loss of adsorbed and intercalated water. In this temperature range, the DSC curve reveals the occurrence of endothermic processes. Dehydroxylation of the inorganic sheets and decomposition of the anion intercalated species happen concomitantly. The DSC curve also indicates the occurrence of an exothermic process during decomposition of the intercalated organic species.

3.5. Fourier Transform Infrared (FTIR) spectroscopy

FTIR analysis is carried out in KBr pellets, pressed from a mixture of 2% of the LDH samples in previously dried KBr. The spectra are recorded over a wavelength range going from 4000 to 400 cm^{-1}. FTIR spectroscopy data provide information about the functional groups and possible interactions between the organic and inorganic parts of the nanocomposites. Identification of the *in situ* polymerization of monomers intercalated into LDH by this technique is difficult because of several overlapping spectral bands.

Figure 9 contains the FTIR spectra of (a) sodium 3-aminobenzoate, (b) pure sodium poly-3-aminobenzoate, and LDH intercalated with sodium 3-aminobenzoate submitted to different treatments [61]. For the pure monomer, the bands (not shown in the figure) at 3408, 3349, and 3223 cm^{-1} are related to $\nu(NH_2)$ symmetric and anti-symmetric stretching, whereas the band at 1628 cm^{-1} is characteristic of $\delta(NH_2)$ symmetric deformation. The bands at 1560 and 1411

cm^{-1} are typical of ν(-COO^-) symmetric and anti-symmetric stretching, respectively. The band at 1312 cm^{-1} is due to ν(C-N) stretching. The bands at 1266 and 1115 cm^{-1} are attributed to δ(NH_2) symmetric and asymmetric deformations. The bands at 776 and 676 cm^{-1} are ascribed to δ(COO^-) out of the plane symmetric and asymmetric deformation. Concerning the polymer, the FT-IR spectrum of pure poly-3-aminobenzoate undergoes significant changes, especially in the area relative to the vibrations of the aromatic ring and the functional group NH_2. The bands due to (-COO^-) in the plane stretching at the 1700 and 1400 cm^{-1}, and (NH_2) out of the plane deformation at 1698, 1634, 1566, 1509 and 1441 cm^{-1} are fairly broad. The broad overlapping bands in the region between 1300 and 1110 cm^{-1}, refer to δ(NH_2) symmetric and asymmetric. Alterations in the spectrum of the polymer are expected because the amine and *p*-methylenes groups of the 3-aminobenzoate molecules interact during polymerization. As for the heat-treated nanocomposites, there is virtually no changes in the profile of the spectra. The bands in the regions between 1700 and 1360 cm^{-1}, related to stretching of the carboxylate group and the aromatic ring are displaced and broader. The bands relative to ν(-COO^-) symmetric and anti-symmetric stretching can be observed in the regions near 1554 and 1384 cm^{-1}. In the region between 1300 and 1110 cm^{-1} there is a shoulder around 1303 cm^{-1} and weak at 1266 cm^{-1}, corresponding to δ(NH_2) symmetric and asymmetric deformation. Analysis of the bands in the regions below 1200 cm^{-1} is highly compromised because of the large overlap of bands with medium and weak intensity. The bands in the regions below 700 cm^{-1} are due to metal-oxygen-metal vibrations occurring in the inorganic host matrix.

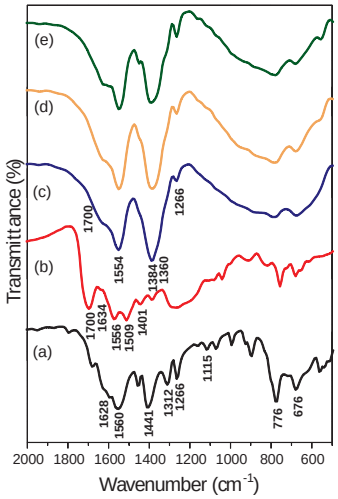


Figure 9. FTIR spectra of (a) sodium 3-aminobenzoate; (b) pure sodium poly-3-aminobenzoate; (c) MgAl-3-aminobenzoate-LDH; (d) MgAl-3-aminobenzoate-LDH with hydrothermal treatment; and (e) MgAl-3-aminobenzoate-LDH heat-treated at 160 °C [61].

3.6. Ultraviolet/Visible (UV-Vis) spectroscopy

The UV-Vis spectra are collected between 200 and 800 nm. Samples are prepared by dissolution of the material in concentrated HCl and subsequent dilution in water.

Figure 10 depicts the UV-Vis spectra pure sodium Poly-3-aminobenzoate and ZnAl-AMB-LDH with different Zn:Al molar ratios(2:1, 3:1 and 6:1) [60].

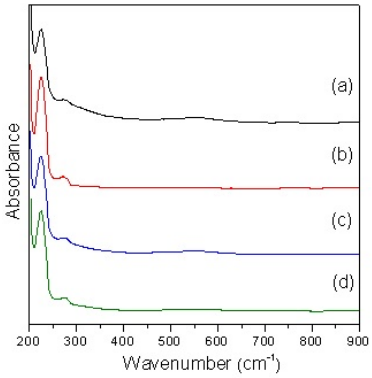


Figure 10. UV-Vis absorption spectra of the materials prepared with (a) pure sodium poly-3-aminobenzoate; (b) Zn_2Al-3-aminobenzoate-LDH; (c) Zn_3Al-3-aminobenzoate-LDH; and (d) Zn_6Al-3-aminobenzoate-LDH.

All the LDH display a band at about 225 nm, after polymerization, the band verified for the monomers is dislocated to lower wavelengths ~215 nm, and a band at ~ 275 nm appears. The latter band is less pronounced for Zn_6Al-3-AMB-LDH prepared by anion exchange in double phase, which is attributed to the n-π* transition due to the presence of non-shared electrons in the COO^- group. After polymerization a peak at ~ 315 nm ascribed to π-π* transition related to conjugation of rings in the polymeric chain is detected. As for the LDH, the first absorption peak intensifies ongoing from the compounds prepared with Zn/Al ratios of 2:1 and 3:1 to 6:1. In the case of the materials prepared by exchange in double phase only for the compounds with Zn/Al ratios of 2:1 and 3:1 the band intensifies. The compound with Zn/Al ratio of 6:1 has the least intense peak.

3.7. Transmission Electron Microscopy (TEM)

The best TEM images are generally achieved when LDHs are dispersed in an epoxy resin, centrifuged, and kept at 70 °C for the 72 h, for drying. After drying, the materials are cut in an ultra-microtome and transferred to hexagonal copper bars appropriated for TEM image acquisition. An alternative approach is to prepare a suspension containing ethanol and LDH. The copper grid is then immersed into the suspension and dried at ambient temperature.

Figure 11 reveals very orderly particles in which the darkest lines represent the inorganic layers and the clearest lines refer to the intercalated conductive polymers [54]. There is good pillaring

of the sheets, with a large sequence of darker lines. The basal spacing value estimated from the TEM images can be compared with the one obtained PXRD analysis.

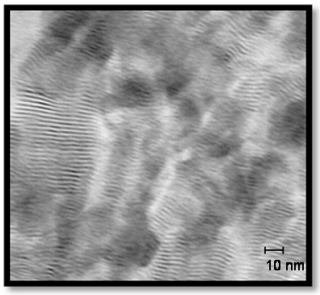


Figure 11. TEM micrographs for ZnAl-4-(1H-pyrrol-1-yl)benzoate-LDH with hydrothermal treatment.

3.8. Scanning Electron Microscopy (SEM)

The morphology of the crystallites and nanocomposite particles can also be analyzed by SEM.

For these analyses, the samples are usually supported on the sample port by powder dispersion on double-sided conductive adhesive tape. Because LDHs do not present enough conductivity for generation of good images it is necessary to cover the samples with gold before the measurements, using a sputter equipment.

Figure 12 shows the SEM images of LDH intercalated with 3-aminobenzoate. There is superposition of the sheets, with formation of aggregates on the surface of the cristallyte [60].

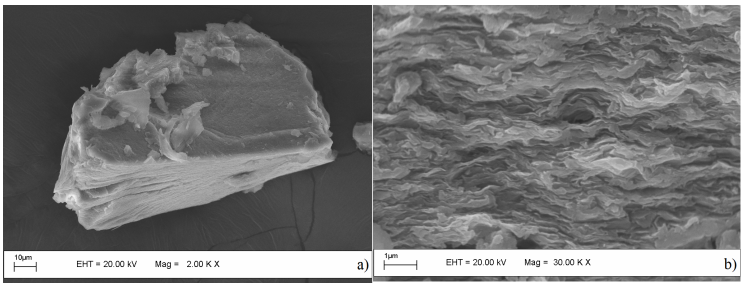


Figure 12. SEM images of ZnAl-3-aminobenzoate-LDH [60].

3.9. Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) experiments are conducted on potentiostats. The supporting electrolyte is 0.1 mol/dm^3 $LiClO_4$ solution, and a conventional electrochemical cell arrangement

involving three electrodes is utilized: Platinum wire as the counter electrode, as the reference electrode (Ag/AgCl/KCl(sat)), and glassy carbon, prepared by dip-coating in an aqueous suspension of monomers intercalated into LDH as the working electrode. The potential of the liquid junction is disregarded. CV experiments enable evaluation of the oxidation and reduction processes of the intercalated monomers. A typical voltammogram of ZnAl-LDH intercalated with 3-aminobenzoate anions is presented in Figure 13. The oxidation process involved in the polymerization of 3-aminobenzoate intercalated into LDH can be noticed. Moreover, Zn^{2+} oxidation can be verified.

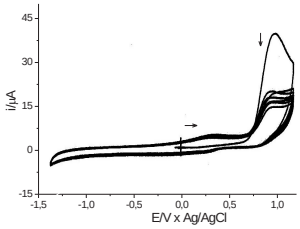


Figure 13. CV for ZnAl-3-aminobenzoate-LDH [60].

There is an irreversible oxidation peak at about 0.960V, and the amplitude of this peak diminishes upon consecutive scanning. This peak is ascribed to 3-aminobenzoate oxidation. A similar behavior has been previously observed for 2-thiophenecarboxylate anions intercalated into ZnAl-LDH.

4. Conclusion

Layered Double Hydroxides (LDHs) are materials whose layered architecture enables separation of the inorganic part (double hydroxide), and the organic portion (conductive polymer), thus culminating in a hybrid composite. The "*growth*" of conductive polymers in limited spaces, like the interlayer region of the LDHs, has been shown to be a very promising method for the improvement of the properties of conductive polymers.

On the basis of literature works, it is possible to deduce that, the guests species (monomers) are generally intercalated in a bilayer arrangement within the LDH layers. In this arrangement, the functional groups of the monomers are directed to the inorganic layer, and the aromatic rings occupy the central region of the interlayer spacing. The nature of the substituent group (aliphatic or aromatic) influences the structural organization and the *in situ* polymerization of the resulting hybrid materials.

During the synthesis, some nanocomposites undergo spontaneous polymerization, while others have to be submitted to thermal or electrochemical treatments to reach polymerization. Monomers containing substituents with aliphatic chains, tend to undergo polymerization in

milder conditions, because the aliphatic chains provide small mobility of the intercalated monomers, thereby faciliting formation of polyconjugated systems. In some cases, thermal treatment may cause collapse of the layered structure, with consequent formation of oxide.

The thermogravimetric analysis data show that, compared with the pure polymer, the LDH-intercalated conducting polymer is more thermally stable. This stability is provided by the inorganic coverage offered by the LDH layers.

In the case of materials intercalated with conducting polymers, there is initial removal of one electron from the polymeric chain, *e.g*, through *p* doping. This results in the formation of an electronic state denominated polaron. Generation of the polaron can also be interpreted as π electron redistribution. Moreover, the formation of this entity is associated with distortion of the polymeric chain, which transforms the aromatic form into the quinoid form. The production of polaron may be also due the presence of electronic state located in the energy region found in the middle of gap. The quinoid structure presents smaller ionization energy and larger electronic affinity than the aromatic form. Polaron is chemically defined as a radical ion of spin = 1/2. As the concentration of polarons increases, they tend to recombine, stabilizing the structure and forming a "bipolaron". "Bipolaron" is defined as a pair of equal diamagnetics dication with spin equal to 0 and equal charges. The formation of "Bipolaron" is associated with strong distortion to the LDH net work.

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