Polymer Interleaved Layered Double Hydroxide: A New Emerging Class of Nanocomposites

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The present paper describes the synthesis and characterization of nanocomposite materials built from the assembly of organic polymers and two-dimensional host materials, particularly reviewing those composed of layered double hydroxide (LDH) inorganic frameworks. When the meaning commonly adopted for nanocomposites is narrowed, the system is constituted of sheets lying on top of each other in which covalent forces maintain the chemical integrity and define an interlamellar gap filled up with the polymer guest. The situation is different from an inorganic filler dispersed into a polymeric matrix. The incorporation of polymer between the galleries proceeds via different pathways such as coprecipitation, exchange, in situ polymerization, surfactant-mediated incorporation, hydrothermal treatment, reconstruction, or restacking. The latter method, recently effective via the exfoliation of the LDH layers, appears to be more favorable, in terms of crystallinity, to capture monomer entities than the whole polymer. The nanocomposites are enlisted according to the preparation pathways. It is found that these multicomponent systems are thermally more stable than the pristine inorganic compounds, leading, for example, to potential applications in flame-retardant composites. A large variety of LDH/polymer systems may be tailored considering the highly tunable intralayer composition coupled to the choice of the organic moiety. The paper concludes with a brief discussion underlining the perspectives. Despite their appeal, the polymer/LDH class of nanocomposites has not yet been extensively studied for applications.

1. Introduction

Currently there is considerable interest for learning how to prepare, to shape, and to improve solids to match the ever-growing demand for multifunctional materials. The simple answer would be to mix together the compounds according to the desired properties, but it is known that an intimate mixture, at a nanometer scale, of the components is needed to reach a combination of properties that are not available in any of the individual parts. The notion of nanocomposites defines organization presenting one of its component of nanometric scale. Thus, this includes systems made of entrapment of species of nanometer size in one dimension such as particles reinforcing the polymeric matrix. Largely developed for such an application, the idea of a reinforcing filler, from the polymer point of view, is not new and remains topical.[1] This is illustrated by silicate-layered materials dispersed as bundles or as small particles into the polymeric matrix, nylon, epoxy, or phenolic resin, poly(ethylene oxide) (PEO), poly(vinyl acetate), polyamide, etc., and defined as organoclays. The layers of the two-dimensional (2D) host pristine materials are propped apart until exfoliation, giving rise to disordered materials. The properties of reinforcement, such as the tensile modulus and elongation at break, were found to be greater when the polymer was present between the sheets of the inorganic matrix rather than

embedded in the inorganic framework, underlining the importance of the interface between the two components.[2]

Because of their highly tunable properties, nanocomposite materials are evaluated for applications in a large number of fields such as those emphasizing mechanical enhancement, gas permeability, or polymer electrolyte.[1e,i,k,3] In this contribution, we present an overview of systems defined as the assembly, strictly speaking, of two components, a polymer, and a 2D host material, more specifically a layered double hydroxide (LDH), and in the case where the bidimensional inorganic arrangement is left unmodified. LDH host materials present the advantage of a large variety of compositions and a tunable layer charge density.[4] Moreover, the LDH sheets are constituted of one polyhedra-made layer, often corrugated, and therefore are more flexible than other bidimensional frameworks such as the 2:1 layered silicate. This has been verified by computing an extended version of the discrete finite-layer rigidity model which includes both intra- and interlayer rigidity effects.[5]

The LDH structure is referred to as the natural hydrotalcite and described with the ideal formula $[M^{II}_xM^{III}_{1-x}(OH)_2]_{intra}[A^{m-}_{x/m}\cdot nH_2O]_{inter}$, where M^{II} and M^{III} are metal cations, A is the anion, and intra and inter denote the intralayer domain and the interlayer space, respectively. The structure consists of brucite-like layers constituted of edge-sharing $M(OH)_6$ octahedra.[6] Partial M^{II} to M^{III} substitution induces a positive

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charge for the layers, balanced with the presence of the interlayered anions. After characteristics of the LDH structure [i.e., its anionic exchange capacity (AEC) and layer charge density] are pointed out, the strategy of its assembly with an organic polymer is referenced in comparison with the general formation of 2D nanocomposite materials. The state of the art in polymer/LDH systems will be presented. This paper concludes by presenting these emerging systems as potential candidates for a large variety of applications as is already exemplified with other nanocomposite parent materials.

2. Synthesis and Description of LDHs

2.1. Synthesis. To better picture the host material, we present its general characteristics induced by the chemical composition and by the nature of the intralayer cations. LDH materials are prepared via the coprecipitation method using M^{II} and M^{III} sources (chloride, nitrate, sulfate, carbonate, etc.) at constant pH.[7] Apart from a few compositions such as [Cu_2Cr] and [Zn_2Cr], most of the LDH materials are prepared under basic conditions. Because carbonate anions present a strong affinity and are difficult to exchange, synthesis is carried out under flowing inert gas. Nevertheless, contamination by carbonate anions on the surface of the crystallites is difficult to avoid. Another method is employed for [Cu_2Cr] which consists of leaving a solution of Cr^{III} cations with finely dispersed CuO oxide slowly reacting.[8] The resulting sample presents an intimate cation distribution different from the sample obtained by the coprecipitation method. The former method is largely preferred for exchange reaction, giving nicely open platelet-like morphology, whereas monolithic chunks are obtained with the coprecipitation method as shown in Figure 1. The comparison to the *sand-rose* morphology of [Zn_2AlCl] is also provided. Other synthetic pathways are adopted: for instance, [Ni_2Fe] is prepared via a three-step method. The building of the slabs of $Ni_{0.70}Fe_{0.30}O_2$ composition is made via the preparation of $NaNi_{0.70}Fe_{0.30}O_2$ sodium nickelate by a high-temperature solid-state reaction; then an oxidizing hydrolysis leads to a layered γ-oxyhydroxide, and a final reduction by adding hydrogen peroxide solution in the presence of the anions gives rise to a LDH material.[9] A particular case is $LiAl_2(OH)_7\cdot2H_2O$ [or $LiAl_2(OH)_6Cl\cdot H_2O$] material, where Li cations diffuse to the open site (one-third of the total octahedra) available in the gibbsite Al-(OH)$_3$.[10] A sol–gel route has also been recently employed using the hydrolysis of alkoxide and acetylacetonate precursors.[11] In this case, the average particle size is found to be smaller and the surface area slightly higher than that of samples prepared by coprecipitation.

2.2. Structure. The structure of LDH material is presented in Figure 2. The versatile intralayer composition is such that many cations are accommodated in the layers of the HDL materials, such as most of the transition metal of the first row (as a divalent cation) combined with Fe, Al, and Ga as trivalent cations.[12] Lately, it has been shown that tetravalent cations such as Zr^{4+} and Sn^{4+} could also be incorporated into the brucite-like LDH layer.[13] This is of importance because the presence of interlayer species is directly related to the net layer charge values, as exemplified with Figure 3 where AEC is given versus the layer charge for some
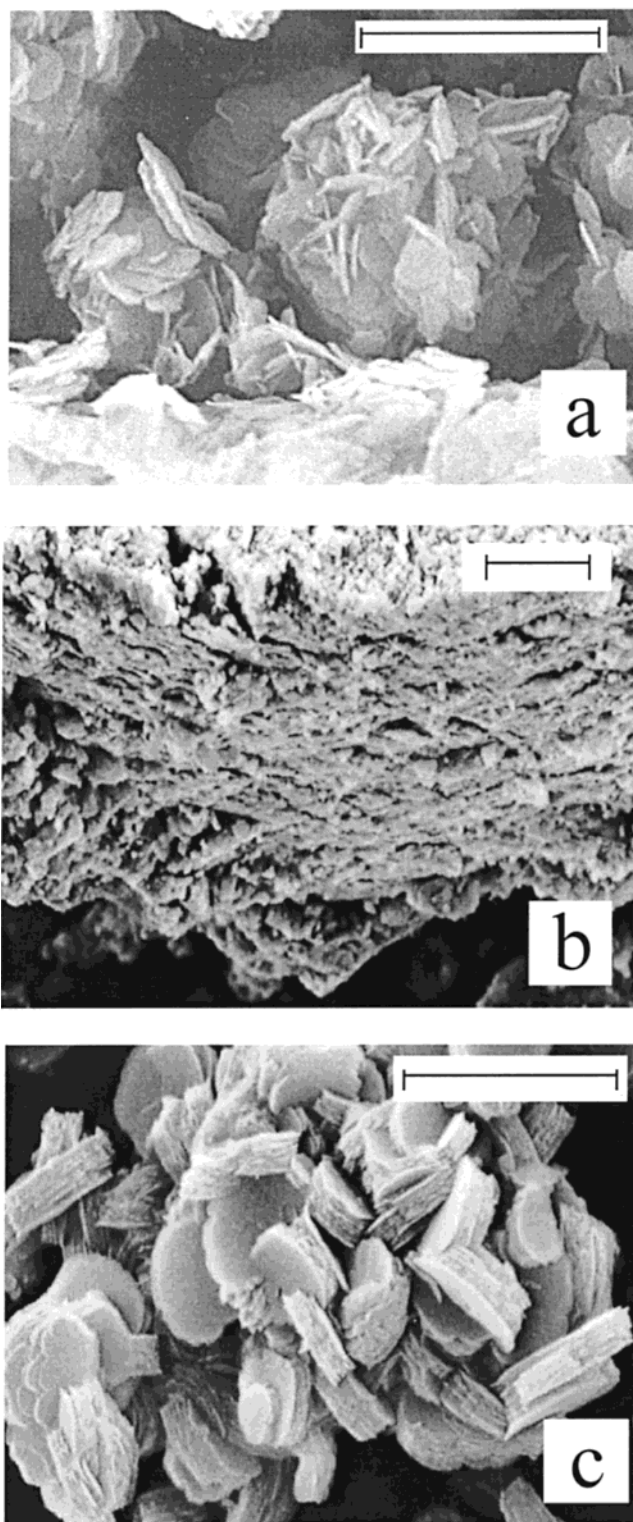

Figure 1. SEM pictures of (a) [Zn_2AlCl] and (b) [Cu_2CrCl] prepared by coprecipitation or the salt and oxide method (c). The bar represents 2 μm. Pictures were recorded with a Cambridge stereoscan operating at 15 kV.

LDH compounds. The data for [$Mg_{1-x}Ga_x$] samples are taken from ref 12a and represented by diamond in the figure. The vacancies of the intersheet domain are not great, taking into account the large packing of anions balancing the layer charge. For comparison, sodium montmorillonite, a cationic clay of composition ($Na_{0.35}K_{0.01}Ca_{0.02}$)($Si_{3.89}Al_{0.11}$)($Al_{1.6}Fe_{0.08}Mg_{0.32}$)$O_{10}(OH)_2$, presents
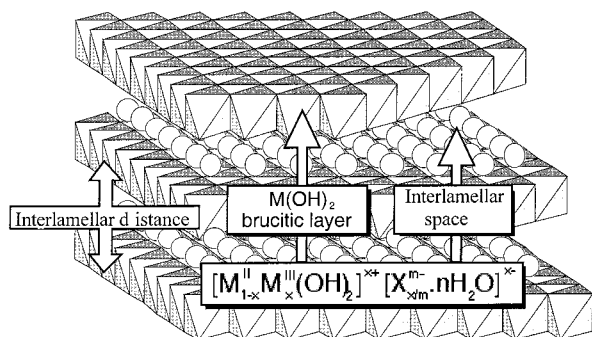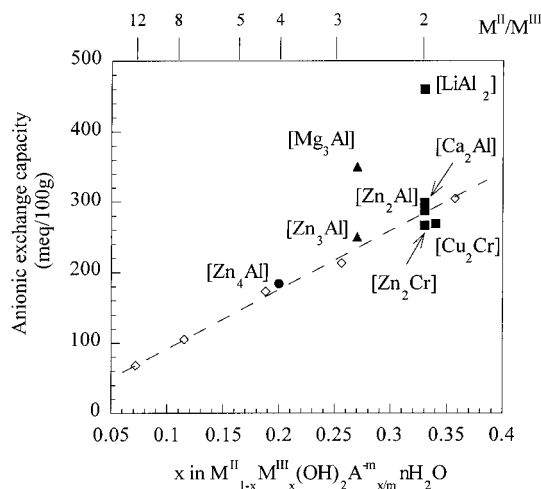
Figure 2. Pictorial scheme of the LDH structure.

Figure 3. AEC vs layer charge for some LDH compositions.

Figure 4. SEM pictures of [$Zn_2AlCO_3^{2-}$] obtained by restacking of the layers. The bar represents 2 μm.

2.4. Particular Properties Suitable To Form Nanocomposites. Partial dehydroxylation occurs after thermal treatment, and LDH materials turn to an amorphous oxide, usually noted as layered double oxide (LDO). Some LDH materials present the property to be recovered, and the oxide reconstructs to the parent LDH on either cooling in air (uptake of carbonate anions) or soaking in water.[18] This technique was used to incorporate large anions such as polyoxometalates.[19]

Nanolayer exfoliation is obviously an advantage to preparing nanocomposites. Some 2D solids present the property (vide supra), such as MoS_2 after reaction of $LiMoS_2$ with water,[20] of layered protonic titanate after reaction with alkylammonium cations,[21] zirconium hydrogen phosphate,[22] oxovanadium phosphate,[23] etc. Low layer charge density, i.e., greater area per charge, is more appropriate for the exfoliation process. Nevertheless, a method was recently reported to exfoliate LDH layers by a two-step approach.[24] An organic spacer molecule is incorporated between the sheets to weaken the attractive forces between layers. Surfactant sodium dodecyl sulfate (Na-DS) was used, propping apart the layers of the LDH compounds. The DS-LDH exchanged phase is then refluxed in a butanol solution. Restacking of the highly pronounced lamellar phase is observed in contrast to the sand-rose morphology of the pristine material (Figure 4).

3. Basic Principles To Obtain a Polymer Intercalated Inorganic Host

2D systems are composed of sheets lying on top of each other in which covalent forces are maintaining the chemical integrity, whereas weak interlayer interactions are present between lamellae. To be completely sandwiched, the organic moiety has to diffuse between the inorganic layers.

There are several possible strategies to incorporate the polymer at the core of the host material as underlined by Schöllhorn in a review paper in 1996,[25] in which the classification of the synthesis was listed as three principal options: (a) intercalation of the monomer molecules; (b) direct intercalation of extended polymer chains in the host lattice; (c) transformation of the host material into a colloid system and precipitation in the presence of the polymer.

an exchange capacity of 108 mequiv/100 g,[14] giving an area per charge of 70 $Å^2$/charge, whereas it is ranges between 25 and 40 $Å^2$/charge for LDH materials. As will be discussed (vide infra), the smaller the exchange capacity (i.e., the layer charge density), the easier the formation of the nanocomposite. A high AEC corresponds to the presence of layers tightly stacked via the attractive forces with the interlayer anions filling the gallery, and this is unfavorable for either an ion-exchange reaction or an exfoliation process.[15] This statement may explain the relatively small number of nanocomposites reported in the literature, added to the fact that each LDH composition leads to a unique material whose properties (exchange, reconstruction, or exfoliation) are not easily transferred from one to another.

2.3. Cation Order. The question of order within the LDH sheets has largely been studied.[16] Cation ordering is observed for [$Zn_2AlSO_4^{2-}$][16g] and $LiAl_2(OH)_7 \cdot 2H_2O$[10] LDH materials. For the former, the order arises from the interlayer anion organization. Cation order is present at a local scale;[16a,c,e] a highly ordered 2D superlattice is, however, rarely observed. The lack of ordering may originate from the large difference in the divalent and trivalent cation radii.[16f]

This is important if one considers the matching host to guest, i.e., the *in-plane* inorganic sheet organization with the size of the monomer unit. This is exemplified with a polyaniline (PANI)/FeOCl system, where the polymer orientation inside the solid is explained by the matching of two −NH− repetitions with a distance of chloride anions along the [101] direction.[17a] This is defined as an endotactic reaction.
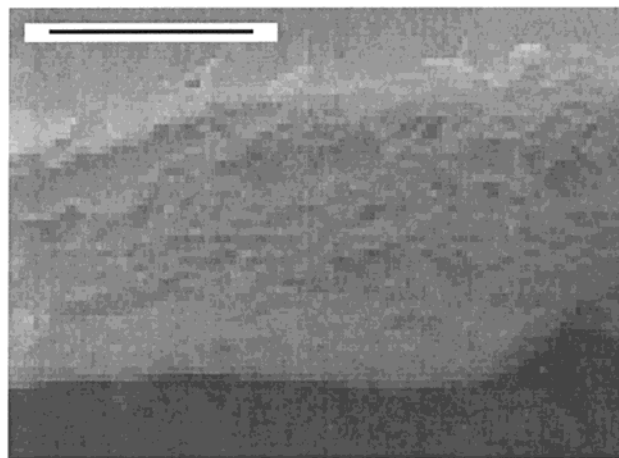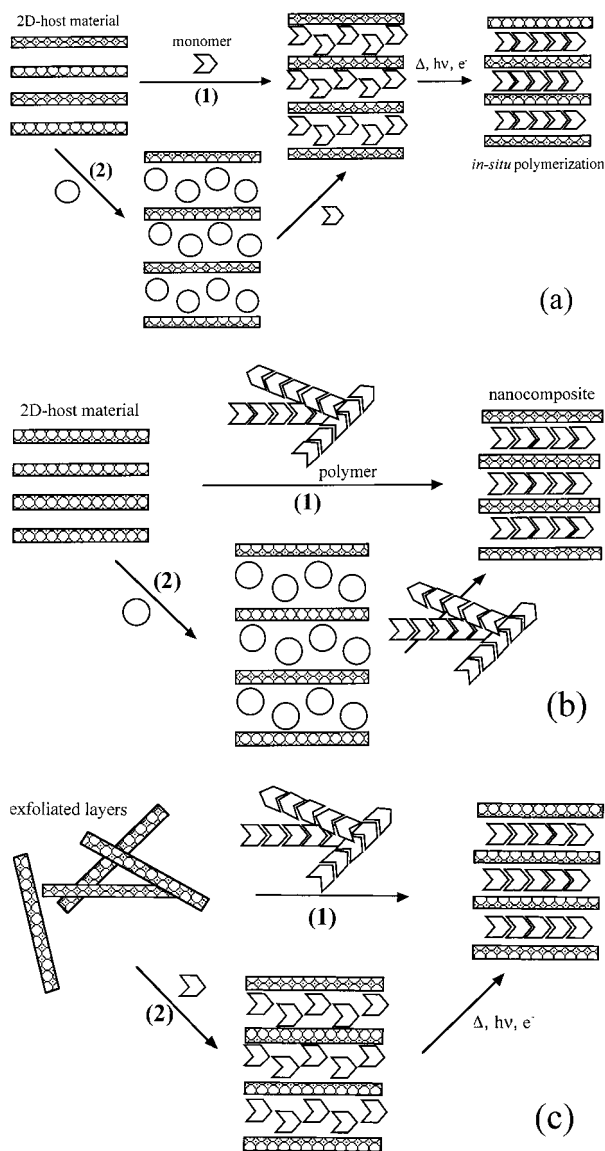
Figure 5. Pathway of nanocomposite preparation by (a) monomer exchange and in situ polymerization, (b) direct polymer exchange, and (c) restacking of the exfoliated layers over the polymer.

Figure 5 illustrates the pathways. For the first pathway (a), the polymerization is occurring between the layers with subsequent thermal, photoinduced, or redox treatment. For a question of size or affinity (hydrophobicity), the incorporation of the guest may be unfavorable. An alternative method (a2) consists of the pre-intercalation of a molecule acting as a spacer, a modifying layer agent, or an in situ reagent. This was illustrated by the incorporation of molecules such as terephthalate in LDH,[26,27] alkylammonium between silicate layers,[28] or hexacyanoferrate for [Cu₂Al] LDH material,[29] respectively.

The second pathway deals with the incorporation of the polymer as a whole between the 2D host material either directly (b1) or after the expansion and chemical change of the layers (b2). Nanocomposite materials are also obtained via the restacking of exfoliated layers. The layer by layer deposition allows one, theoretically, to overcome the diffusion problem when dealing with polymer. Unfortunately, the method is only applicable

to the 2D host whose layers can be delaminated. As for pathway a, an alternative (c2) may be employed: restacking of the layers on the monomer, thus avoiding the problem of compatibility of size and/or of charge density between the polymer chain and the single layer. The in situ polymerization (a) method is used for the incorporation of various monomers such as aniline, pyrrole, nylon from the polycondensation of ε-aminocaproic acid, methyl methacrylate, vinylbenzene sulfonate, vinylpyrrolidone, vinyl acetate, etc. In situ polymerization is limited by two factors: (i) the distance from monomer to monomer when it is strongly anchored (or grafted) to the host matrix, i.e., its degree of freedom; (ii) the condition that the polymerization (temperature, pH, or redox reaction) must leave the layered structure intact. The so-called "reductive intercalative polymerization" developed by Kanatzidis et al. consists of the incorporation of conductive polymers into a host material. The latter may be an oxidizing bidimensional matrix such as vanadium pentoxide xerogel, leading to nanocomposites of different nature, polymer/V_2O_5 [polymer = polythiophene (PTH), PPY, PANI].[30] During the process, a concomitant polymerization is occurring via the redox reaction provided by V^{5+} cations. For a no-oxidizing matrix, an external agent such as $FeCl_3$ or $(NH_4)_2S_2O_8$ is used, as illustrated, for instance, with the polymerization of aniline or pyrrole into $HNbMoO_6$,[31] $FeOCl$,[32] α-$RuCl_3$,[33] MoO_3,[34] and graphitic oxide.[35] Solventless oxidative polymerization was recently reported for hectorite clay exchanged with Cu^{2+} and Fe^{3+} cations.[36] Thermal postsynthesis treatment is employed to induce the monomer linkage, as exemplified with the insertion of the precursor *p*-xylene-α-dimethylsulfonium chloride into MoO_3 hydrated bronze[37] or with the incorporation of ε-aminocaproic acid into α-ZrP, leading to a nylon nanocomposite after treatment at 200 °C under nitrogen.[38]

Direct intercalation of polymers can be achieved via dispersion of clay mineral in dissolved polymers such as PEO/montmorillonite[14] or PEO/MoO_3[39] systems. The former presents 2D ionic conductivity due to the motion of the intracrystalline cations confined in PEO. It was found that, even for dispersed phases such as an epoxy/clay system, the key was to load the clay gallery with a hydrophobic tail surfactant.[11] To overcome the incompatibility between the polymer and the host, the nature of the interlayer space is often modified; the lipophilization of the clays by alkylammonium cations reduces the surface polarity of the silicate layers, enhancing the affinity between the silicate and the matrix. The so-called "refined guest displacement" and "surfactant-mediated pathway" are employed for the poly(vinylpyrrolidone) (PVP)/kaolinite system via kaolinite/ammonium acetate precursor[40] and for the incorporation of poly(*p*-phenylene) into molybdenum bronze,[41] respectively.

Finally, polymer inclusion is reported for nanocomposites PANI/MoS_2,[42] poly(ethylene glycol) (PEG), PVP, and PEO/$NbSe_2$.[43] The formation proceeds with the restacking of the layers in an appropriate solvent. Intercalation of polymers into the interlayer space of smectites has been extensively studied. It is, however, difficult to avoid reaggregation of the layers when the polymer interacts with the fully delaminated smectite

colloid.[44] Some examples illustrating the nanocomposite formation are enlisted in Table 1.

4. Polymer LDH Nanocomposites

Polymer/LDH nanocomposites can be referred to as organoceramics. A large variety of anionic polymers have been introduced between the layers of hydrotalcite- or hydrocalumite-type materials. FTIR and CPMAS solid-state ^{13}C NMR spectroscopies are commonly used to confirm the presence of the organic moiety in the nanocomposites. The preparation is carried out via several different pathways.

4.1. In Situ Polymerization. The incorporation of a polymer between the LDH sheets may be achieved by the in situ polymerization. For instance, an acrylate/[Mg$_2$Al] LDH hybrid material, obtained via exchange with the interlayered anions (Cl$^-$ or NO$_3^{2-}$), is further polymerized after thermal treatment at 80 °C. The basal spacing was found to slightly decrease from 13.8 Å to 13.4 Å.[45] The IR spectroscopy provides information on the polymerization with the disappearance of the C=C vibration band. It is noteworthy that the carbonate LDH phase does not react with acrylate. Acrylic acid was also intercalated in the lamellar structure of an iron-substituted nickel LDH material.[46] In this study, potassium persulfate is used as an initiator for the polymerization process. The resulting phase was although partially exchanged by SO$_4^{2-}$. Insertion of the polymer leads to a phase presenting a basal spacing of 12.6 Å thinner than that of an acrylate-intercalated monomer phase (13.6 Å). This was explained by the absence of electrostatic repulsion between the C=C double bonds. Insertion of conjugated polymers into the LDH framework was first reported by Challier and Slade.[29] Terephthalate- and hexacyanoferrate-exchanged [Cu$_2$Cr] LDH phases are used as host matrixes for the oxidative polymerization of aniline. The reaction performed under reflux conditions gives rise to a rather poorly defined material with a basal spacing of ≈13.5 Å. From IR diagnostics, the authors conclude that PANI polymer is present as short chains of oligomers under its emeraldine base form. The nanocomposite material was found to exhibit a poor temperature stability.

An alternative consists of incorporation of a soluble anionic monomer such as aniline-2-sulfonate or metanilic acid (3-aminobenzenesulfonic acid, H$_2$NC$_6$H$_4$SO$_3$H). Polymerization of the monomer requires conditions less drastic than those for aniline, giving rise to a relatively well-ordered system.[47] In situ polymerization performed at 200 °C in air induces a reorientation of the organic part as evidenced by a decrease of the basal spacing. The structure of the nanocomposite PANI/Cu$_2$Cr sustains much a higher temperature than the pristine material, which transforms into Cu$_2$OCl$_2$ at 200 °C.

The contraction of the interlayer distance is also noted for the in situ polymerization of vinylbenzene sulfonate between [Zn$_2$Al] LDH sheets (Figure 6a). The methods listed in Figure 5 are evaluated for the poly(styrene sulfonate) (PSS)/Zn$_2$Al nanocomposite system (vide infra).[48] Following a preswelling method described by Drezdon,[26] a terephthalate form of [Mg$_2$Al] LDH is used as a starting material to capture the negatively charged polystyrene (PS) oligomers.[49] The authors found that the dianions are rapidly ion-exchanged for the oligomers.
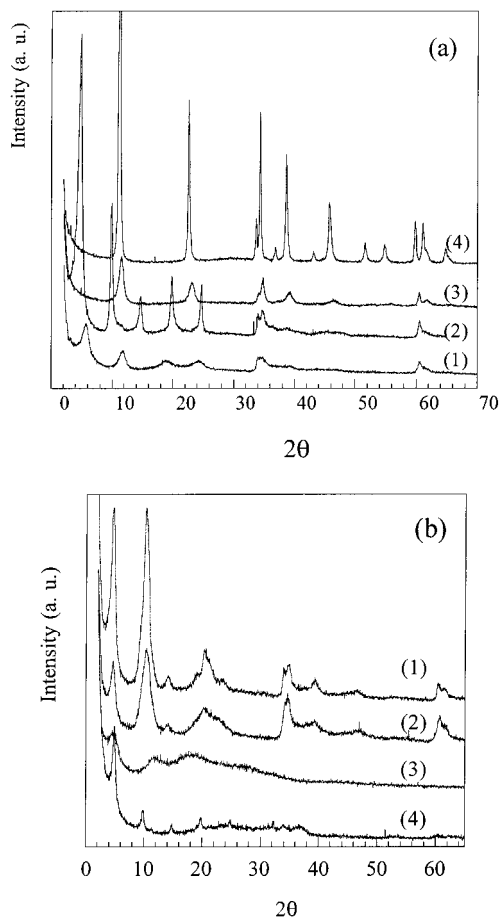

Figure 6. XRD patterns of Zn$_2$Al/PSS nanocomposites obtained via the following: (a) In situ polymerization (1). The diagrams of the monomer-exchanged phase (2) and of the pristine material at room temperature (3) and at 150 °C (4) are also reported for comparison. (b) Polymer direct exchange (1), reconstruction (2), or restacking of the layers over the polymer (3) or the monomer (4). A diffracted beam monochromator Cu Kα source and steps of 0.04° with a counting time of 4 s are used. Patterns are offset for clarity.

4.2. Direct Intercalation. Poly(α,β-aspartate) was inserted in the [Mg$_3$Al] LDH phase by in situ thermal polycondensation or by direct intercalation as a cosolute in the basic reaction solution.[50] The condensation process proceeds from the aminosuccinic acid via a polysuccinimide intermediate which rearranges to give polyaspartate at 220 °C. It was found that the basal spacing decreases during the condensation process from 11.1 to 9.0 Å, giving an available space of only 4.2 Å for the accommodation of the polymer. A larger space (10.3 Å) is observed in the case of the direct synthesis, but this is associated with a change of the trivalent to divalent cation ratio from 3 to 1.33.

Incorporation of PSS was extensively studied. The presence of polymer between a [Zn$_2$Al] LDH is evidenced on the X-ray diffraction (XRD) diagrams, showing an increase of the interlayer distance from 7.74 to ≈21 Å. This is an indication of a substantial uptake of polymer between the sheets and corresponds to an increase of the available gallery height (up to 15.9 Å), consistent with the presence of a bilayer of PSS paving either side of the LDH sheets.[48] PSS/LDH nanocomposite materials are also prepared by a templated reaction;[51] i.e., polymer
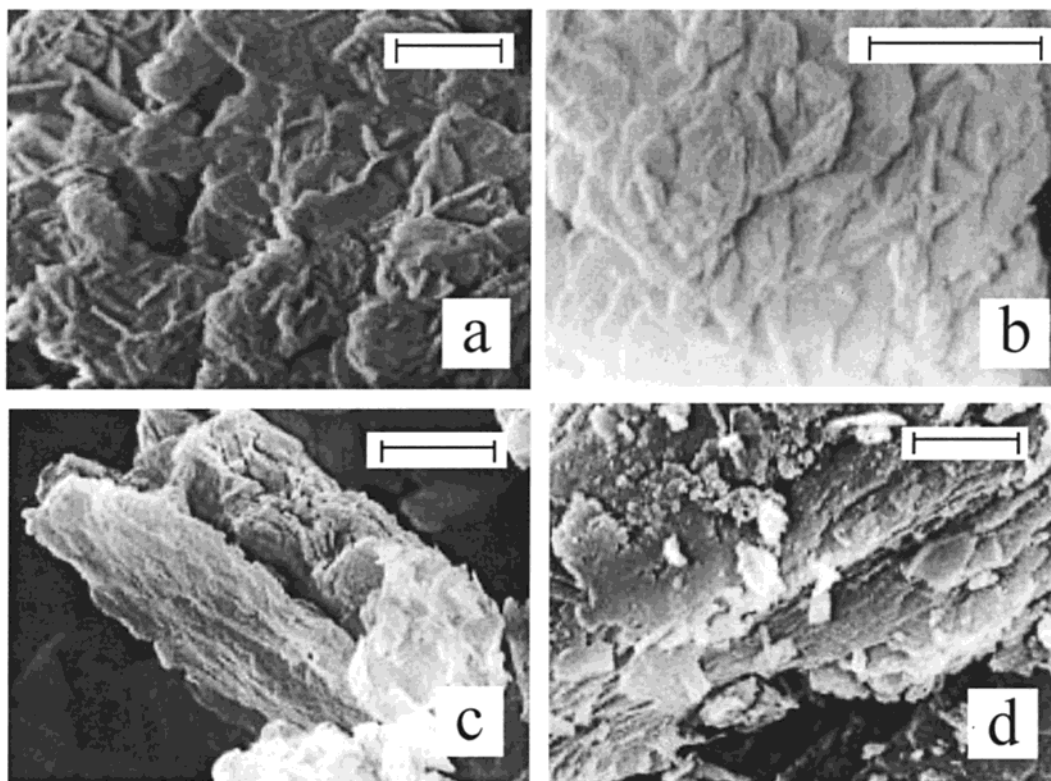
Figure 7. SEM pictures of Zn$_2$Al/PSS nanocomposites prepared via (a) in situ polymerization, (b) reconstruction, (c) direct exchange, and (d) restacking. The bar represents 2 μm.

is introduced during the coprecipitation using a [Mg$_2$-Al] or [Zn$_3$Al] LDH material.

The insertion of polymer affects not only the crystallinity but also the dimension and morphology of the pristine host material. Scanning electron micrographs (SEM) of PSS/LDH nanocomposites (Figure 7) are compared to the pristine material (Figure 1). The *sandrose* morphology of the pristine materials disappears to the profit of a lamellar arrangement. The sheets are more or less crumpled depending on the pathway. The layers are on the order of a few nanometers in size, much smaller than those of the nanocomposites prepared with the templating method.[51] Other systems are prepared by the templated reaction such as those composed of poly(acrylic acid) (PA) and/or poly(vinyl sulfonate) (PVS) with hydrotalcite[52,53] or hydrocalumite[54] type compounds. Recently, we have reported the direct intercalation of long-chain polymers such as PEG/alkenylsulfonic acid between [Cu$_2$Cr] layers.[55]

4.3. Restacking Process. Illustrated with the PSS/Zn$_2$Al system, the restacking of layers over the polymer gives rise to poorly defined material. A few harmonics are only present after the encapsulation of the monomer (Figure 6b).[48] Although, it is well suited for the uptake of monomer, which can be further polymerized.

When an amorphous LDO is contacted with a solution containing PSS, it is possible to obtain a nanocomposite, which presents similarities in terms of crystallinity and morphology with the phase prepared by a direct exchange (Figure 6b).[48] For the first time, the reconstruction method was found to be suitable for the incorporation of molecular guests as cumbersome as polymer chains.

From the information reported in the literature and our recent studies, it is clear that the organic to inorganic framework assembly is highly sensitive to the preparation conditions as illustrated by the difference in stacking regularity in the nanocomposite phases. X-ray absorption spectroscopy experiments performed on the nanocomposites show that the intralayer cation order is mostly unchanged with the incorporation of polymer, except in the case of the exfoliation–restacking of the layers.[24b] The mentioned nanocomposites are listed in Table 2. The influence of preparation for the PSS/Zn$_2$Al system is evidenced with the SEM pictures (Figure 7).

The [Mg$_2$AlCO$_3$$^{2-}$] LDH phase exhibits a positive electrophoretic mobility, whereas the PSS/Mg$_2$Al nanocomposite presents a negative one, indicating that the surface properties are dominated by the anionic sulfonate end group.[52] This is in agreement with PSS adsorption measurements,[48] where PSS adsorbed on the surface of the particles was found to represent 10% of the total exchange capacity of the pristine material.

The poly(vinyl acetate) (PVA)/Ca$_2$Al layered structure was found to be stable up to a temperature of 400 °C.[54] The authors speculated that the nature of the interface between the organic and inorganic components may be the reason of the high thermal stability. The organoceramic transforms at high temperature into an inorganic solid of composition different from that for the pristine host material. SEM pictures show how the nanocomposite is degraded in temperature (Figure 8); the organic residue encompasses the inorganic crystallites, thus preventing the Ca(OH)$_2$ crystallization.

5. Potential Applications and Perspectives

The constrained environment provided by the host material is interesting for many applications such as

Table 1. Examples of Polymer/2D Host Systems Illustrating the Pathways of Nanocomposite Formation[a]

LDH 2D matrix	polymer	pathway	d (Δd) (Å)	ref
$V_2O_5 \cdot nH_2O$	PANI	a	13.8	30
FeOCl	PPY	a	13.2 (5.2)	32
α-ZrP	nylon	b	12.2	38
montmorillonite	poly(vinylpyridine) (1,2 form)	a	15.2	2
MoS_2	PANI	c	10.37	42a
$NbSe_2$	PVP, PEO, PEG	c	24.0, 19.6, 18.8	43
$[(Li/Na)H_2O]_{0.25}MoO_3$ bronze	poly(p-phenylene)	b	11.96 (5.0)	41
graphitic oxide	PANI, PVA	a	11.52 (4.9)	35a,b

[a] The intersheet distance is noted when available. PANI = polyaniline, PPY = polypyrrole, PTH = polythiophene, PVP = poly(vinylpyrrolidone), PEO = poly(ethylene oxide), PEG = poly(ethylene glycol), and PVA = poly(vinyl acetate).

Table 2. Polymer/LDH Nanocomposite Classification (See Text)[a]

LDH 2D matrix	polymer	pathway[b]	d (Å)	ref
$Cu_{0.66}Cr_{0.33}(OH)_2(terephthalate)_{0.17} \cdot nH_2O$	PANI	a	13.3	29
$Cu_{0.66}Al_{0.33}(OH)_2(hexacyanoferrate)_{0.17} \cdot nH_2O$	PANI	a	13.5	29
$Ca_{0.66}Al_{0.33}(OH)_2(OH)^-_{0.33} \cdot H_2O$	poly(vinyl alcohol)	a	18	54
$Mg_{0.74}Al_{0.26}(OH)_2(CO_3)^{2-}_{0.13}(NO_3)^-_{0.006} \cdot 0.32H_2O$	poly(α,β-aspartate)	a, b	9.0	50
$Mg_{0.66}Al_{0.33}(OH)_2(CO_3)^{2-}_{0.17} \cdot nH_2O$	PSS	cop	20.8	51
$Zn_{0.75}Al_{0.25}(OH)_2(CO_3)^{2-}_{0.13} \cdot nH_2O$	PSS	cop	21.6	51
$Mg_{0.66}Al_{0.33}(OH)_2(terephthalate)^{2-}_{0.17} \cdot nH_2O$	PS	a	23.2	49
$Mg_{0.66}Al_{0.33}(OH)_2(CO_3)^{2-}_{0.17} \cdot nH_2O$	PA, PVS	cop	12.0, 13.1	52
$Zn_{0.75}Al_{0.25}(OH)_2(CO_3)^{2-}_{0.13} \cdot nH_2O$	PA, PVS	cop	12.4, 13.3	53
$Co_{0.75}Al_{0.25}(OH)_2(OH)^-_{0.13} \cdot nH_2O$	PVS	cop	13.3	53
$Ca_{0.66}Al_{0.33}(OH)_2(CO_3)^{2-}_{0.17} \cdot nH_2O$	PA, PVS, PSS	cop	12.4, 13.1, 19.6	53
$Mg_{0.66}Al_{0.33}(OH)_2(NO_3)^-_{0.33} \cdot nH_2O$	polyacrylate	a	13.4	45
$Ni_{0.7}Fe_{0.3}(OH)_2(SO_4)^{2-}_{0.17} \cdot nH_2O$	polyacrylate	b	12.6	46
$Zn_{0.66}Al_{0.33}(OH)_2(Cl)^-_{0.33} \cdot 0.63H_2O$	PSS	a−c	15.6, 21.2, 19.8	48
$Cu_{0.66}Cr_{0.33}(OH)_2(Cl)^-_{0.33} \cdot 1.14H_2O$	PEG	b	30.1	55
$CU_{0.66}Cr_{0.33}(OH)_2(Cl)^-_{0.33} \cdot 1.14H_2O$	PEG/alkenylsulfonic acid	b	37.4	55
$Cu_{0.66}Cr_{0.33}(OH)_2(dodecylsulfate)^-_{0.33} \cdot nH_2O$	PANI sulfonate	a	14.2	47

[a] Vinylic polymers: poly(acrylic acid) (PA), poly(vinyl sulfonate) (PVS), poly(styrene sulfonate) (PSS). [b] cop = *templating* reaction.
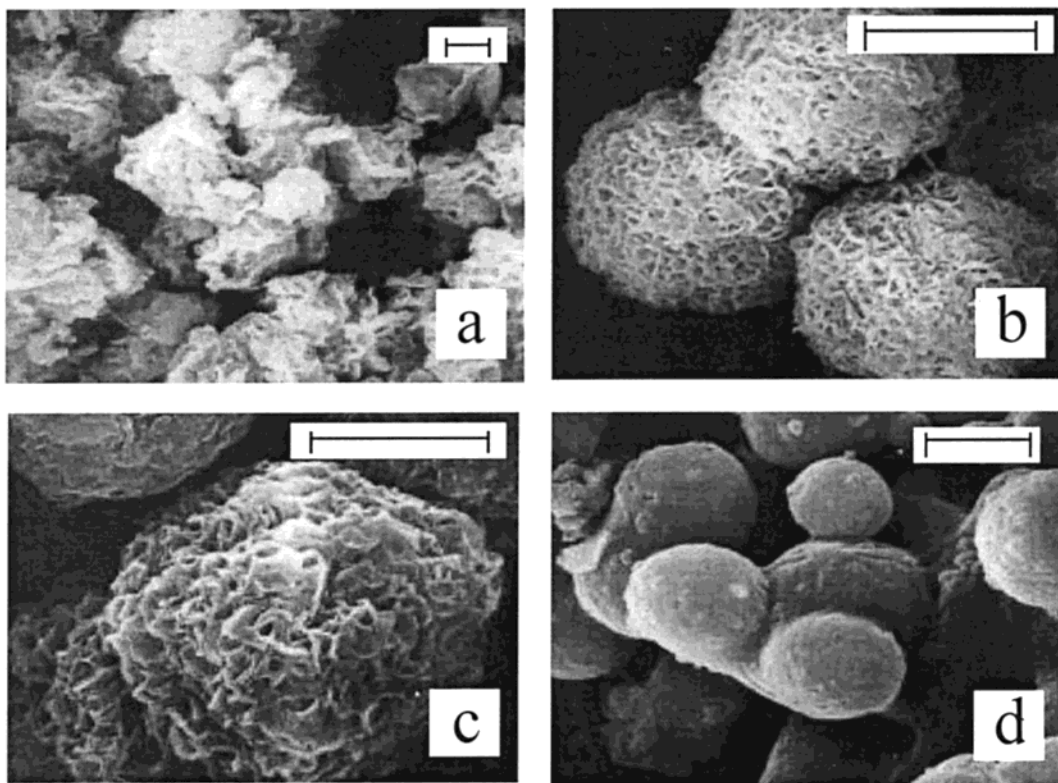

Figure 8. SEM pictures of PVA/hydrocalumite at (a) room temperature, (b) 300 °C, (c) 500 °C, and (d) 1000 °C.[43] The magnification bars in the micrographs correspond to 2 μm.

those regarding the protection of the polymer from the UV degradation or as flame retardant. For instance, polymer-layered silicate nanocomposites were found to present a unique combination of reduced flammability and improved physical properties. This has been exemplified with poly(propylene-*graft*-maleic anhydride) and PS-layered silicate nanocomposites using montmorillonite and fluorohectorite.[56] The authors found that the

heat release rate was significantly reduced for intercalated and delaminated nanocomposites. Despite the presence of hydroxyl groups and of water molecules, polymer/LDH systems have never been studied, to our knowledge, for such an application, although the protection of the polymer from heat requires the development of environmentally friendly, inexpensive flame-retardant additives.[57]

Biomolecules such as DNA could be stabilized in the interlayer space of [Mg$_2$AlNO$_3$]. The hybrid material is pH-sensitive and therefore can be considered as a gene reservoir.[58] This opens new opportunities for the LDH framework. In the approach of building new biocompatible composites, intercalation of polymers such as poly(vinyl alcohol) (PVA) was studied in calcium silicate hydrate.[59a] Other biomimetic materials are reported for the 2D host structure[59b] but also for more complex materials such as mesoporous silica.[60]

Making use of the interlamellar opening of clays, highly oriented graphite was obtained from the carbonization of poly(acrylonitrile).[61a] It was found that water molecules of the mineral act as a pore former during the process.[61b] Several examples as 2D clay host structures are reported in the literature such as the taeniolite molecular template,[61c] bentonite pillared with [Al$_{13}$O$_4$-(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ and treated with pyrene,[61d] and sepiolite.[61e] Controlled porosity is obtained from synthetic PVP-layered magnesium silicate hectorite via calcination.[62]

Some of the intercalated polymers present excellent physical properties such as conductive properties (PANI), insulator (PS), or ion-gate property [polypyrrole (PPY)] but are difficult to process because of their lack of mechanical strength. Numerous studies are reported in the literature concerning the use of conductive polymers as capacitor or rechargeable battery materials[63] or in electrochromic windows.[64] Conjugated polymer interleaved into a 2D host structure promotes generally the ion diffusion, as observed for PANI or PPY/V$_2$O$_5$ nanocomposites,[65] and also presents an electroactive response on a larger voltage domain than the polymer itself.[66] Aniline was directly electropolymerized between the sheets of a montmorillonite,[67] and a polymer/clay PPY/montmorillonite composite shows promising properties for both sensor and electrolysis application.[68] Tungsten oxide and PANI films were studied for electrochromic applications, taking advantage of the anodic coloration of PANI and the cathodic coloration of the inorganic framework.[69] To our knowledge, applications for the LDH/polymer nanocomposites have not yet been developed. The conjugated polymer/LDH systems, however, may be of interest for electrocatalytic applications.

We believe that nanocomposites offer useful new properties compared to conventional materials, properties unattainable by either the organic or the inorganic component. A large volume of research has been devoted to this field but little on the polymer/LDH system. Known to be suitable for a large variety of applications as diverse as protonic conductors,[70] clay-modified electrodes,[71] batteries,[72] or photochromic[73] materials, catalysts,[74] or waste-carriers materials,[75] LDHs have the potential to rise this new challenge.

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