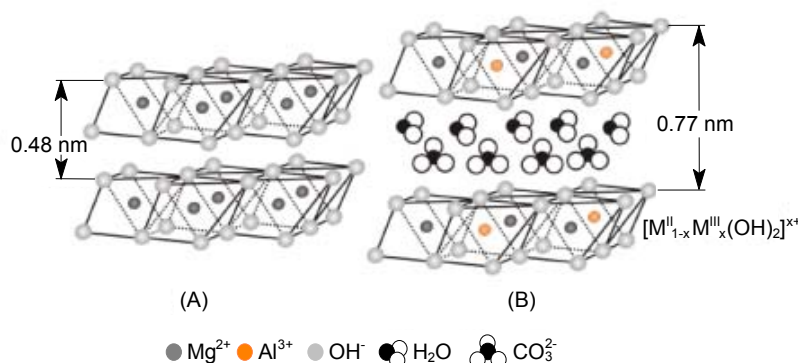


Layered double hydroxides: noble materials for the development of multi-functional nano-hybrids

Layered double hydroxides (LDH), auch als anionische Tonminerale bekannt, werden seit längerem in der Katalysertechnik und in verschiedenen biologischen und medizinischen Anwendungen eingesetzt. Die Nutzung von LDH als multifunktionelle Nanofüllstoffe ist in den letzten Jahren in der Polymerforschung forciert worden. Dazu trugen die positive Ladung der Hydroxidschichten, die im Gegensatz zu den weit verbreiteten Schichtsilicaten eine anionische Modifizierung erfordert, die chemische Aktivität, die eine Kopplung organischer Moleküle an die anorganische Oberfläche ermöglicht, die hohe einstellbare Ionenaustauschkapazität und die Wasserabspaltung bei höheren Temperaturen besonders bei Mg-Al-LDH wurden hergestellt, modifiziert und in polymerer Matrix nanoskopisch verteilt. Für unpolare Matrices (z.B. PE) zeigte sich, dass ein Verstärkungseffekt aufgrund des hohen Modifikatorbedarfs nicht erreicht werden konnte, der bei polaren Matrices wie carboxyliertem Nitrilbutadienkautschuk (XNBR) deutlich nachgewiesen werden kann. Gezeigt werden konnte, dass LDH ein effektiver Co-Flammhemmer in Polyolefinen mit einer Metallhydroxid-Basisflammhemmung ist.

Introduction

Layered double hydroxides (LDHs) are a class of anionic clay materials well known for their catalytic application, which includes reactions involving basic catalysis, hydrogenation, oxidation, support for Ziegler-Natta catalysts, etc. They are also widely used in biomedical field for the treatment of peptic ulcers, controlled drug release, biosensor, etc. In the recent years, lots of attention has been drawn to a new area of application of LDHs namely development of multifunctional LDH nano-hybrids for polymer materials. To investigate the potential of LDHs, for this new application their structure and properties should be understood first.



The general chemical formula of LDHs is written as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, where M^{II} is a divalent metal ion, such as Mg^{2+} , Ca^{2+} , Zn^{2+} , etc, M^{III} is a trivalent metal ion, such as Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , etc and A^{n-} is an anion, such as Cl^- , CO_3^{2-} , NO_3^- , etc. The anions occupy the interlayer region of these layered crystalline materials.

Keywords

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Fig. 1:
Schematic representation
comparing the crystal structure of
brucite (A) and LDH (B)

Although a wide range of values of x is claimed to provide LDH structure, the pure phase of LDH clays is usually obtained for a limited range as $0.2 < x < 0.33$. The structure of LDHs can best be explained by drawing analogy with the structural features of the metal hydroxide layers in mineral brucite or simply the $\text{Mg}(\text{OH})_2$ crystal structure. Brucite consists of a hexagonal close packing of hydroxyl ions with alternate octahedral sites occupied by Mg^{2+} ions. The metal hydroxide sheets in brucite crystal are neutral in charge and stack one upon another by Van der Waals interaction. The interlayer distance or the basal spacing in brucite has a value of about 0.48 nm. In LDH, some of the divalent cations of these brucite-like sheets are isomorphously substituted by a trivalent cation and the mixed metal hydroxide layers, $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}$, thus formed acquire a net positive charge. This excess charge on the metal hydroxide layers is neutralized by the anions accumulated in the interlayer region. The interlayer region in LDHs also contains some water molecules for the stabilization of the crystal structure. The presence of anions and water molecules leads to an enlargement of the basal spacing from 0.48 nm in brucite to about 0.77 nm in Mg-Al-LDH. A schematic representation comparing the brucite and the LDH structures is shown in Fig. 1.

LDH as nanofiller

In recent years, there is a growing interest in using LDH as novel nanofiller for polymers and in that sense it is a competing material to layered silicates, the most commonly used nanoclays. The characteristics that make LDH suitable as nanofiller are its layered structure and readily exchangeable interlayer anions with large organic species. So, principally, LDH can be treated similarly as layered silicates to make polymer nanocomposites. But, LDH has distinct advantages over layered silicates, like

1. Chemically active: its makes grafting of organic species on inorganic layers [1]
2. Thermally unstable: the endothermic decomposition above decomposition temperature of many polymeric materials helps in improving flame retardancy through active participation in flame inhibition.
3. Cationic layer charge: can be modified by wide range of anionic species starting from anionic surfactants to large anionic metallic clusters (polyoxo metalates) or anionic metal complex [2].
4. Large anion exchange capacity: theoretical AEC (at $\text{M}^{\text{II}} : \text{M}^{\text{III}} = 2 : 1$) is greater than 400 mmole/100g LDH.

The reactivity of LDH to wide range of organic and inorganic anionic species makes it an ideal material for designing nanohybrids with diversified applications some of which will be discussed in the following sections.

Synthesis and intercalation behavior of LDH

LDH is can be synthesized by different methods, such as co-precipitation of M^{2+} and M^{3+} ions followed by hydrothermal treatment, homogeneous precipitation using urea or urea releasing agent, co-hydrolysis followed by co-precipitation of the metal alcoxide. Hydrothermal crystallization method involves the crystallization of amorphous $\text{M}^{\text{III}}_2\text{O}_3$ precursor in presence of a suitable $\text{M}^{\text{II}}\text{O}$, etc. In our laboratory, we are mainly using homogeneous precipitation method.

LDH materials have unique property of regenerating its structure from its oxide form, which is commonly referred as *memory effect*. When LDH is heated above 450 °C for several hours, it is converted into a mixed oxide. This oxide on dispersion in an aqueous solution of the interlayer anion (for example, CO_3^{2-} , Cl^- , etc) can regenerate the original LDH structure. This has been demonstrated in Fig. 2. The wide angle X-ray scattering (WAXS) pattern and the FT-IR spectra of LDH and its regenerated form indicate that they have virtually the same chemical and crystal structures.

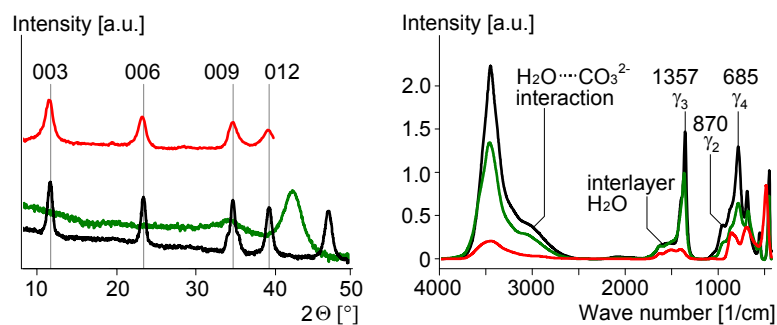


Fig. 2: WAXS pattern (left) and FTIR spectra (right) of LDH (—), its oxide form (CLDH, left —) and CDH, right —) and its regenerated form (LDHR —)

Using the memory effect we investigated the intercalation behavior of Mg and Al containing LDH (Mg-Al-LDH) with several anionic surfactants, such as alkylsulfonate with several chain lengths, phosphates, carboxylates, etc. The oxide form of LDH is usually dispersed in the aqueous solution of the surfactants and the regeneration takes place with the surfactant anions as the intercalating anions in the LDH structures. The WAXS analysis of these organically modified LDH shows the increase in the interlayer distance in proportion to the chain length of the hydrocarbon tail of the surfactant (Fig. 3a). At higher chain length, e.g. with C_{18} tail, formation of double layer by the anions in the interlayer region is also observed. The successful intercalation (Fig. 3b) of these different anions shows indeed LDH can be effectively intercalated with various organic functionalities.

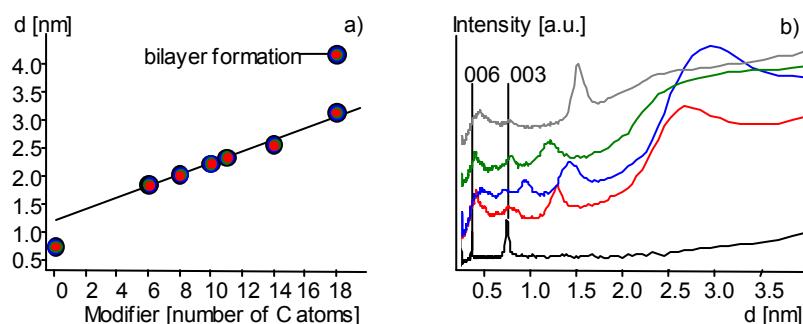


Fig. 3: Variation of the interlayer distance (d) of the organically modified LDH depending on the size (a) and nature (b) of the surfactants. In (a) surfactants are alkyl sulfonates and in (b) the surfactants are dodecyl sulfate (DS), dodecylbenzene sulfonate (DBS), laurate and bis (2-ethylhexyl) hydrogen phosphate (BEHP): LDH —, LDH-DS —; LDH-DBS —; LDH-laurate —; LDH-BEHP —. The values in (a) were determined from the 1st (●), 2nd (◐), 3rd (◑), and 4th (◒) reflection order.

Polymer/LDH nanocomposites

Organically modified LDHs (organo-LDH) have been used for the synthesis of polymer nanocomposites. The melt compounding technique shows that these LDH can be dispersed in nanoscale with partial exfoliation of the LDH layers in polymer matrix [3, 4]. The optimization of the processing conditions and proper selection of the organic modifier can lead to further improvement in nanofiller dispersion.

Fig. 4 shows how the LDH-DBS (dodecylbenzene sulfonate-modified LDH) particles are dispersed in two polymer matrices with different polarities. It is obvious that in a polar matrix (carboxylated nitrile rubber, XNBR), a higher degree of exfoliation of LDH layers

is observed than in a non-polar matrix (polyethylene). It is the high surface charge density ($0.25\text{-}0.33\text{ C}\cdot\text{m}^{-2}$) that makes a high degree of exfoliation of LDH difficult in later. The organic modification is thus a necessary requirement not only to increase the interlayer distance, but also to improve the compatibility of LDH with polymer matrix by reducing its surface energy [5]. Like a classical nanofiller LDH can improve the mechanical properties of polymer matrix significantly. For example, in matrices like epoxy, poly(methyl methacrylate) (PMMA), etc., a small amount of organo-LDH significantly improves the mechanical properties in comparison to the unfilled matrix [6, 7]. We have also observed similar effect in XNBR. Besides acting as reinforcing nanofiller, organo-LDH can also serve as an active flame-retardant. For example, it can substantially reduce the heat release rate during combustion. These aspects, i.e. reinforcing and flame-retardant nature of organo-LDH, are demonstrated in Fig. 5.

Fig. 4:
Nature of dispersion of LDH in (a) polyethylene and in (b) carboxylated NBR (black arrows indicate intercalated primary LDH particles and red arrows indicate exfoliated particles)

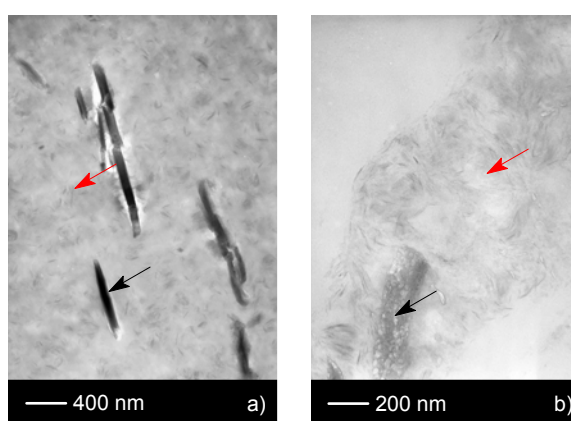
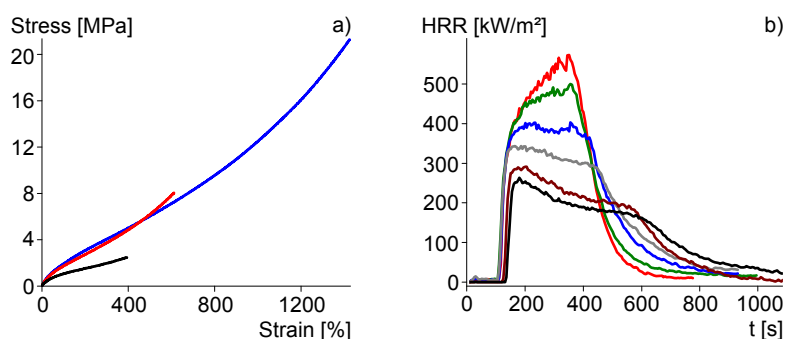


Fig. 5:
LDH as a reinforcing nanofiller for polymer matrix (a) in XNBR matrix (XNBR —; XNBR + 5 phr LDH —; XNBR + 10 phr LDH —), and as a flame-retardant (b) in polyethylene (PE + 2.43 wt-% LDH —; PE + 4.72 wt-% LDH —; PE + 6.89 wt-% LDH —; PE + 8.95 wt-% LDH —; PE + 12.75 wt-% LDH —; PE + 16.2 wt-% LDH —; HRR = heat release rate)



LDH as reactive nanofiller

LDH is very active to polymers having acidic functional groups, especially carboxylic group. This has been clearly observed in case of XNBR, which has carboxylic functionality pendent on its backbone. These acid groups react with the hydroxyl groups on LDH sheets. Even though LDH is organically modified, such reaction is not obstructed. The evidence of such reaction is obtained from the FTIR and dynamic mechanical (DMA) analysis of XNBR/LDH nanocomposites as shown in Fig. 6. In the FTIR spectra of the nanocomposites, the appearance of an additional peak around 1614 cm^{-1} indicates the formation of carboxylate salt in the system. This is further supported by the DMA observation, where a secondary $\tan\delta$ peak that appears at higher temperature (absent in absence of LDH) indicates the possible existence of ionic clusters in the nanocomposites. These clusters melt at higher temperature resulting in an additional $\tan\delta$ peak during DMA analysis. The effect of such ionic interaction

between LDH and XNBR is also apparent from Fig. 5. The nanocomposites with 5.0 and 10.0 phr organo-LDH show significantly higher mechanical strength in comparison to the corresponding gum vulcanizate.

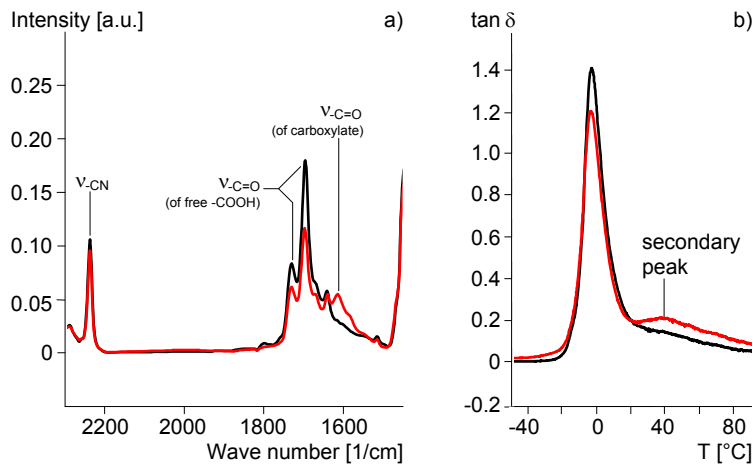


Fig. 6: The evidence of chemical interaction organo-LDH and functionalized polymer (XNBR): (a) FTIR showing the formation of salt and (b) DMA showing the possibility of ionic structure in the composites (XNBR —; XNBR + 5 phr LDH —)

LDH as a flame-retardant

Although the uses of LDH clay as heat stabilizer and acid scavenger in halogenated polymers (such as poly(vinyl chloride), PVC) are well known [8], its use, as inorganic flame-retardant is not very common. The flame-retardant characteristics of LDH clays originate from their $Mg(OH)_2$ like chemistry, which involves endothermic decomposition with the liberation of water vapor and often carbon dioxide. The residue of such combustion is the metallic oxide that impedes the burning process by reducing the oxygen supply to the fresh surface beneath. The early report on the flame-retardant application of LDH was published by Miyata et al [9]. The idea was to add hydrotalcite (naturally occurring LDH clay) either in unmodified or in surface treated form at high concentrations (> 50 wt%) in polymers, like polyolefins, polystyrene, nylon, polycarbonate, etc. to obtain flame-retardant compositions. In fact, such high concentrations often provided industrial acceptable flammability ratings (such as UL94 V0), but the mechanical properties of the final composites were drastically affected.

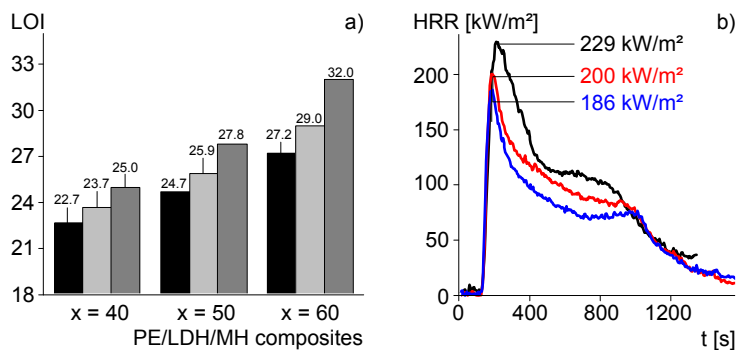


Fig. 7: Organo-LDH as flame-retardant synergist for $Mg(OH)_2$ (MH) in polyethylene (PE). (a) the limited oxygen index (LOI) value improves significantly in PE/MH composite MH amount (represented by x wt%) is partially replaced by organo-LDH. (b) the lowering of heat release rate (HRR) is also observed in the combined system for x = 40 wt% (0L40M —; 5L35M —; 10L30M —)

The treatment of LDH clays as flame-retardant as well as a nano-filler can be a potential development in this regard. In the recent years, many reports have been published that highlight the improved thermal and flammable properties of LDH clay based polymer nanocomposites. Recently, Zammarano and co-workers [10] have reported synthesis of self-extinguishing epoxy/LDH nanocomposites. They have also observed a synergistic effect between LDH

clay and ammonium polyphosphate in such nanocomposites, where reduction of APP concentration from about 30.0 wt% to about 16.0-20.0 wt% can be tolerated in presence of a small amount of LDH without sacrificing the flammability performance.

We have also investigated flame-retardant behavior of organo-LDH alone and in combination with other flame-retardants [11]. Fig. 5 demonstrates how organo-LDH alone can reduce the heat release during combustion of polyethylene/LDH nanocomposites. The synergistic flame-retardant effect between organo-LDH and other conventional flame-retardants has also been investigated in details. For example, with conventional $Mg(OH)_2$ (a microscopic filler) satisfactory flame-retardancy can be achieved at much lower filler concentration than that when $Mg(OH)_2$ is used alone as the flame-retardant [12]. Fig. 7 shows that a high LOI value and lower heat release rate can be achieved at relatively lower concentration of this mixed system i.e. organo-LDH and microscopic $Mg(OH)_2$. The similar synergistic effect is also observed in thermoplastic polyurethane, where ammonium polyphosphate (APP) and a char former (pentaerythritol derivative) are used as the conventional flame-retardant components. By introducing 3-5 wt% organo-LDH in this *flame-retardant package*, the concentration of APP and the char former can be reduced significantly without sacrificing the flame retardant behavior.

Organo-LDH as UV and photo-stabilizer

The cationic nature of the LDH crystal layers enables the use as modifier of an enormous diversity of functional anions and its wide possibilities for carrying out practically this modification, not only through direct ion exchange reactions, but also via calcination-regeneration or even by *in situ* synthesis, in both cases in the presence of adequate modifying anions. One group of these modifying species can be UV and photo-stabilizers with nucleophilic or anionic functionalities that can interact with positive LDH layer. The objectives of intercalating these chemicals within LDH layers are the improvement of their stability, preventing leaching out or loss from a system and improvement of their biocompatibility.

For example, nanohybrids obtained through the intercalation of organic UV-ray absorbents cinnamic acid and *p*-methoxycinnamic acid in LDH structure show high oxidative stability and excellent UV absorption capacity [13]. Similarly, when a commercial red pigment C.I. Pigment 52:1 is intercalated in LDH, the nanohybrid shows much improved thermostability and photo-stability as compared to the free pigment [14]. This kind of hybrid materials can have application in designing sunscreen formulations and other skin care products [15].

LDH in controlled drug release

LDHs are now being investigated for their potential use as reservoir and carrier for bio-molecules for improving their stability, controlled release, etc. For example, Choy et al. have demonstrated that different bio-molecules such as DNA, nucleoside mono- and triphosphate, etc, into Mg-Al-LDH [16, 17]. These molecules can be more efficiently transferred into cell, when they are administered in their LDH hybrid forms. LDHs are also suitable host materials for various anionic pharmaceutical chemicals. For example, nonsteroidal anti-inflammatory drugs, like ibuprofen, fenbufen, diclofenac, etc. have been successfully intercalated in LDH. It has been observed that the *in vitro* release of these drugs

from the LDH-drug hybrid is much slower than that in case of a commercial formulation based on phosphate buffer [18, 19].

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