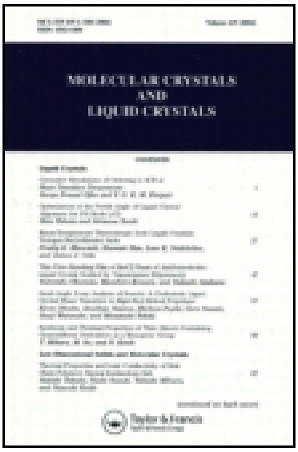

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Layered Double Hydroxides (LDH): A Multifunctional Versatile System for Nanocomposites

A. Leuteritz [a], B. Kutlu [a], J. Meinl [a], D. Wang [a], A. Das [a], U. Wagenknecht [a] & G. Heinrich [a]
[a] Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

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Layered Double Hydroxides (LDH): A Multifunctional Versatile System for Nanocomposites

A. LEUTERITZ,* B. KUTLU, J. MEINL, D. WANG, A. DAS, U. WAGENKNECHT, AND G. HEINRICH

Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

Layered Double Hydroxides gained tremendous research efforts in the last years as a filler for polymer nanocomposites similar to montmorillonite in order to increase barrier properties, improve mechanical properties and reduce flammability. Due to its broad variety in composition and possibility to organically modify the layers LDH might be used in very different applications. This summary intends to show possibilities of integration of additional functionalities apart from the benefits of LDH as platelet decomposing like the classical flame retardant magnesium hydroxide, by selecting a specific metal combination, by fine tuning structural features and by selecting an organic modification with a functionality thus providing a true added value to filler for nanocomposite applications.

Keywords Conductivity; flame retardancy; layered double hydroxide; photostability; vulcanization

Introduction

Research on layered minerals derived from hydrotalcites or layered double hydroxides is a growing field in nanocomposites. In recent years, there has been increasing interests in layered double hydroxides (LDHs) or so called synthetic anionic clays and their intercalated compounds. These materials have wide combinations with metal species and are mostly well known for their catalytic activities in organic synthesis. The other potential applications for LDH materials include controlled drug release, improving heat stability and flame retardancy of polymer composites, water treatment, adsorbent, additive for PVC, etc. The use of anionic clays for preparing polymer nanocomposites is a rather new field of research. Compared to natural clays, LDH has the advantage of structural homogeneity, which could be tuned during their synthesis. Besides, high bound water content and high reactivity towards organic anionic species make them suitable in many specific applications. The idea of using LDH clays as suitable materials for polymer nanocomposite synthesis is based on their two main characteristics: one is their layered crystalline geometry with various intercalating anionic species and the other is the ability to interchange these inter-layer anions with much larger organic anionic molecules. The latter is very important as the pristine layered clay minerals are not suitable for penetration of giant organic molecules into their

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*Address correspondence to A. Leuteritz, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany. Tel.: +49(0)3514658378; Fax: +49(0)3514658290. E-mail: leuteritz@ipfdd.de gallery space unless the original interlayer distance is increased through organic modification, additionally changing drastically the interphase characteristics between polymer and inorganic layer. These materials can be very interesting to industry as they combine features of well-established fillers like $Mg(OH)_2$ and properties of nanocomposites based on, e.g., montmorillonite. Again the challenge is to disperse LDH in rather nonpolar polymers, as the LDH itself is polar due to the high number of hydroxyl groups. Further, the composition of the layer is adjustable, allowing fine tuning of organic ions in the interlayer as well as a selection of different metal species to form the inorganic layers. Last, the organic modification itself can bear an additional functionality, e.g. light absorption, biological activity and others. Therefore the objective of this work is to show the possibilities of nanocomposites based on LDH with truly integrated functions in one nanoscale additive.

Structure of LDH

The crystallographic structure of LDH is best described starting from magnesium hydroxide crystallizing as brucite. Brucite consists of a hexagonal close packing of hydroxyl ions with alternating layers of octahedral sites occupied by Mg^{2+} ions. Thus, the layers are charge balanced and stacked one upon another by Van der Waals forces. By substituting a part of the divalent magnesium ions with trivalent aluminium ions, the layer gains a net charge, which must be compensated. The charge compensation is achieved by ions in the interlayer (Fig. 1a). In case of carbonate as interlayer ion, the natural occurring mineral hydrotalcite is derived and therefore the whole group of natural and artificial minerals is often referred to as hydrotalcite-like materials. These materials have the chemical composition $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}\ A^{n-}_{x/n} \cdot yH_2O$, where M^{II} and M^{III} represent the layer forming cations and $A^{n-}_{x/n}$ represents the interlayer ion.

Although, the structure is described with divalent and trivalent cations, there are minerals included in this group using the same stacking principle with other valences covering now almost all metals of the periodic table. In the case of Mg-Al LDH with carbonate ions in the interlayer a typical pattern in Wide Angle X-ray Scattering (WAXS) is found indicating an interlayer distance of 0.77 nm (Fig. 1b).

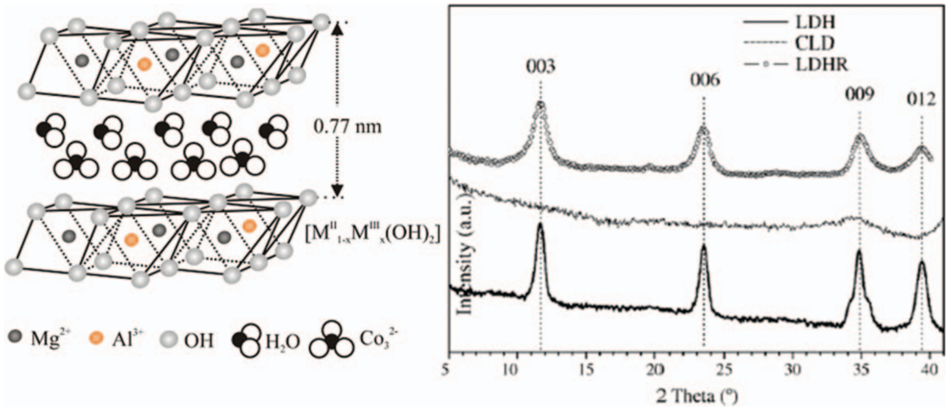

Figure 1. Schematic description of LDH (a) and WAXS pattern of hydrotalcite, and its calcined and regenerated form (b)

Synthesis of LDH

For synthesis of LDH the homogeneous precipitation method is widely used. In this method an appropriate salt solution is heated together with urea under reflux. The urea decomposes slowly to form carbonate ions and ammonia, generating basic conditions for the precipitation of the LDH [1]. Depending on the actual conditions different results are obtained. Both the amount of urea and the reaction time strongly affect the properties of the precipitate as shown in Fig 2a-d.

All precipitates feature good crystallinity as indicated by the presence of first and higher order reflections in the WAXS experiment. However, SEM investigation reveals that the layered structures are covered by an obviously amorphous phase. This amorphous phase hinders simple ion exchange reaction as the interlayer ions are no longer accessible for the acidic activation necessary for organic modification [2]. Even the metal combination can change the result of homogeneous precipitation, as in some cases the decomposition mechanism of the urea is changed [3]. The big advantage of the homogeneous precipitation method is that heating up one solution in simple equipment is sufficient.

The second widely used and almost universally applicable method for preparation of LDH is the coprecipitation method. In principle a solution of the desired metal ion combination is continuously dropped into the reaction flask. Simultaneously a base is added to maintain the pH-value at an appropriate value, in case of Mg-Al LDH pH 9 to 10. The more constant the conditions are kept, the better the resulting LDH material

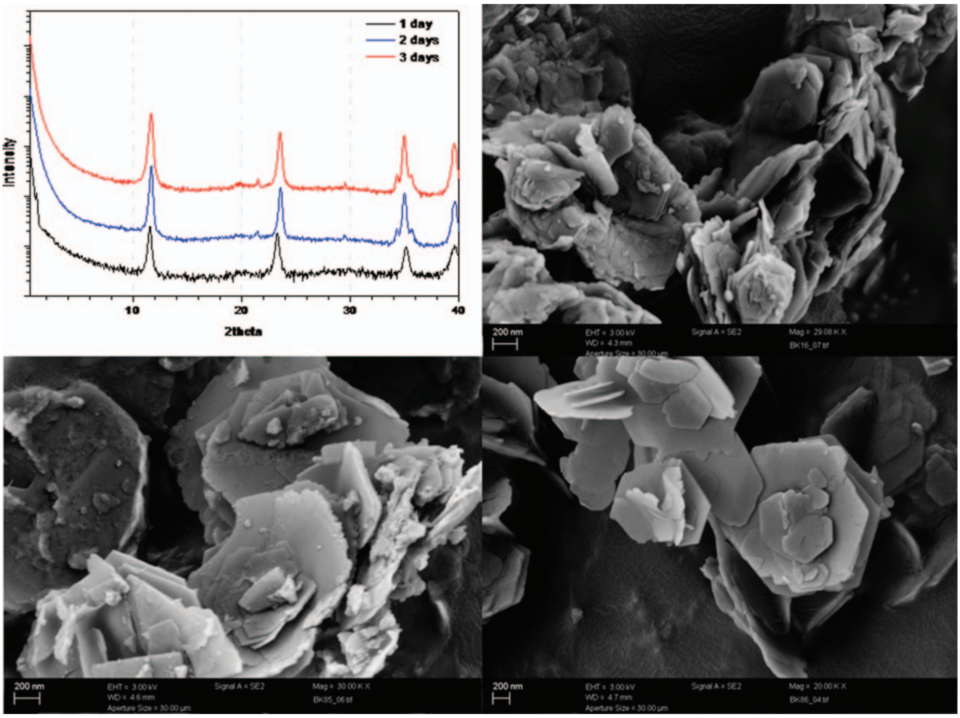

Figure 2. WAXS pattern and SEM images of LDH reacting one, two and three days in homogeneous precipitation method.

[4]. Additionally, this method allows the organic modification of the LDH layer in a one-step reaction [5]. Nevertheless the size of the pristine layers achieved with coprecipitation method is rather small, which might be overcome by post-synthesis hydrothermal treatment [6], but this can also lead to the destruction of the LDH [7].

Organic Modification of LDH

The simplest method to modify LDH is to use an ion exchange reaction. The starting LDH is just stirred for several hours in a solution of the desired anion and filtered off followed by intensive washing. However, while several ions like chloride and nitrate are easily exchanged others like carbonate are difficult [8]. Surprisingly, some salts of organic acids such as camphor sulfonic acid can be easily exchanged into samples derived from homogeneous precipitation, whereas they cannot be exchanged into samples from coprecipitation. This observation is currently under investigation and might derive from the size of the LDH platelets [9]

A special feature of LDH is the ability to regenerate its structure after calcination at 450°C. During the calcination process the LDH loses water and carbon dioxide and its crystalline structure. By dispersing this calcined form into a solution of inorganic or organic salts the structure is recovered (see Fig. 1b) with the respective anion of the salt instead of the carbonate, thus allowing an organic modification with a wide variety of ions [10].

Use of Organomodified LDH, Some Examples

A straight forward approach of using LDH materials is to substitute classical flame retardants magnesium hydroxide (HT) and aluminium trihydrate (ATH) by LDH. As LDH decomposes similarly to HT and ATH and additionally has a layered structure, an advanced reduction of flammability using LDH in polyolefins was expected in comparison to montmorillonite as passive flame retardant, when the LDH is dispersed at a nanometer level. Costa et al. [11] investigated in detail the properties of Mg-Al-LDH polyethylene nanocomposites. The thermal and flammability properties of MgAl-LDH, modified with dodecylbenzene sulfonate, and prepared by two-step melt compounding in a twin screw extruder using a maleated polyethylene as compatibilizer are summarized in [12]. Although polyethylene is a nonpolar, matrix exfoliation was achieved as shown by wide angle X-ray scattering and transmission electron microscopy. Even at low filler content, a strong reduction of the peak heat release rate (PHRR) was observed in cone calorimeter tests. Nevertheless, using the limited oxygen index method as the measure, flammability only decreased with filler contents beyond 15%.

A series of Mg-Al-LDH was synthesized in which the magnesium content was partly or totally substituted by Zn. Oleate was selected as interlayer ion to facilitate clay dispersion in nonpolar matrices. These organo-LDHs were melt-compounded with maleic anhydride grafted polypropylene as compatibilizer and polypropylene as matrix polymer. The peak heat release rate is a key factor for fire spreading. In general a large decrease was observed for all nanocomposites. Interestingly, composition also played an important role in the flammability of the nanocomposites.

The performance of nanocomposites with varying chemical composition was also compared. Increasing the substitution of Mg by Zn decreased the peak heat release rate from 1137 kW/m^2 for the pure Mg-LDH to 992 kW/m^2 for a Mg-Zn-Al-LDH having equal amounts of Mg and Zn and finally reached 757 kW/m^2 in case of the nanocomposite based on pure Zn-Al-LDH. Compared to the pure matrix this is a reduction of nearly 70% [13]. Further investigation about the role of the metal ion in the composition is currently performed in our lab.

Organomodification is a prerequisite for dispersing LDH by melt compounding in a nonpolar matrix polymer. The role of the organic anion in the interlayer was studied in order to selects the right LDH organomodifier for the polymer matrix [14]. It was shown that the dispersion and exfoliation depended on the length of the alkyl group of the respective organic acid salt, and additionally on the type of acid (sulfate, sulfonic, carboxylic, phosphonic, etc.) as well as the anion exchange capacity (i.e. the ratio of trivalent to divalent cations present in the LDH).

A more sophisticated approach to LDH utilization is to use the organic modification to introduce an additional functionality into LDH nanocomposites beyond the reduction of flammability, improving mechanical properties according to Halpin-Tsai or reducing permeability due to the tortuous path model. Instead of intercalating a simple organic acid into the LDH interlayer, the use of functional acids was investigated. Examples include integrating flame retardants (e.g., polyphosphoric acid derivatives), dye molecules, antimicrobial active acids or polymerizable acids for conductive polymers. A great variety of organic dye molecules are available in acid salt form and they can be easily intercalated into the interlayer of LDH. The inorganic layer leads to an anchoring effect, preventing the extraction of UV-protecting agents, e.g. from sun screen formulations [15]. Additionally the shielding effect of the LDH prevents the oxidative degradation of the organic dye molecule and drastically increases its thermal stability [16]. Recently, it was shown that this stabilisation effect is sufficient to allow melt compounding of dye bearing LDH, which then still exhibited good colour properties. Obviously in this case a total exfoliation is not desirable [9]. For some applications added value from modification derives from electrical conductivity, besides the reinforcement or flame retardant effect of the filler. For example in high value body panels electric conductivity of the polymer composite is necessary to prevent colour differences from off-line and inline lacquered parts of car bodies. Another such application comes from the cable industry. Here the outermost layer of the insulator has to be conductive to a certain extent in order to keep down times low in case of maintenance of high voltage cables. Due to safety regulations such kinds of cables have to be flame protected in indoor applications. The proof in principles was achieved by incorporating polyaniline into LDH layers. In this way flame retardancy and conductive properties were simultaneously introduced into polyethylene [17].

Even though the characteristics of the LDH layer and the use of functional acids to modify the LDH in the interlayer are already used to incorporate a further function, the possibilities of the chemical composition of the LDH inorganic part has not yet explored to a significant extent. Taking advantage of the chemical composition of the inorganic LDH layer has been achieved in rubber nanocomposites by using Zn-Al-LDH, organically modified with stearic acid. A truly multifunctional additive was created by dispersing this type of LDH. It was found that the conventional vulcanization package consisting of ZnO and stearic acid could be omitted totally. Figure 3 compares vulcanization curves of a nitrile rubber obtained in a moving die rheometer with a standard curing package (stearate plus ZnO) or with the stearate modified LDH (Zn-Al as well as Mg-Al). In case of the Zn-Al and stearate modified LDH the curing reaches the same extent, but much faster than the other samples, even outperforming state-of-the-art vulcanizing systems.

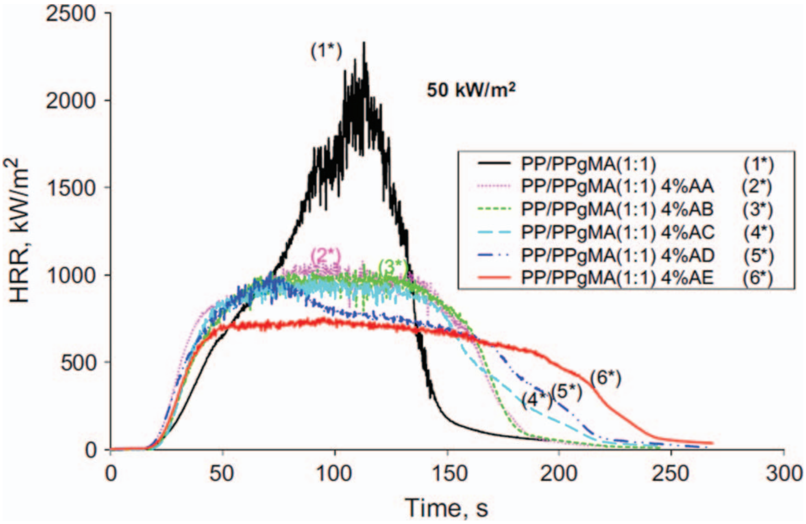

Figure 3. Heat release rates derived from cone calorimeter tests of polypropylene LDH nanocomposites based on Mg-Al-LDH right and Zn-Al-nanocomposites with varying composition [13].

Despite about 100 years of research on tyres, the mechanism of vulcanisation is not yet fully understood. Yet we found an accelerated vulcanization system applicable to different rubber types. Vulcanization with stearic acid modified LDH comparable to standard curing packages with partially improved properties for the vulcanizate can be achieved at a zinc content of only 10% of that of the original curing package as indicated by rheometric curing curves shown in Fig. 4 [18].

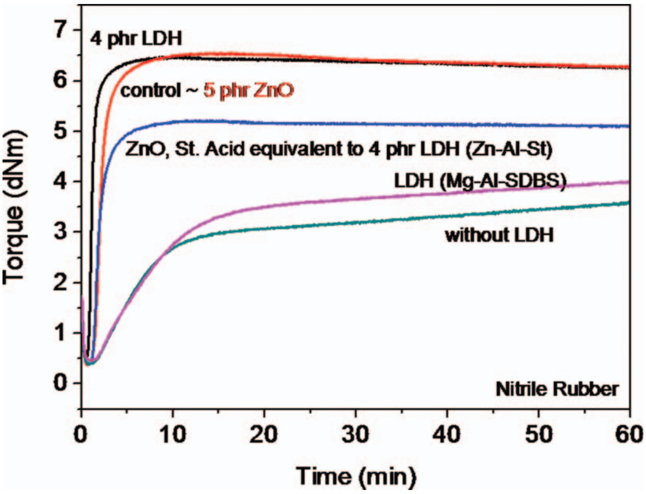

Figure 4. Rheometric (MDR) curing curves of nitrile rubber at 160 °C; The curing pakage is comprised with 1 phr TMTD and 0.5 phr sulphur. Control compounds contain 1 phr TMTD, 0.5 phr sulfur, 5 phr zinc oxide and 2 phr stearic acid.

Conclusion

Value-added polymer and rubber nanocomposites can be prepared with Layered Double Hydroxides by integrating several functionalities into the nanofillers via the chemical composition of the inorganic layer forming cations, by using the features of the layer decomposition, by using their action as reinforcing and barrier generating abilities due to their layered structure or by introducing a functional interlayer ion for rendering the inorganic particle organophilic and adding properties from the organic moiety simultaneously. Therefore LDH can be considered as a truly multifunctional additive.

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