Received: 13 January 2023 | Revised: 11 April 2023 | Accepted: 17 April 2023
DOI: 10.1002/pol.20230025

REVIEW

JOURNAL OF POLYMER SCIENCE WILEY

Tailoring materials for their need: Sustainable layered double hydroxide polymer composites

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Abstract

Layered double hydroxides (LDHs) are popular functional fillers increasingly used in composite materials. They can be designed via metal and anion selection as well as the specific processing method to prepare structures with desired functional properties. This makes LDHs suitable for many different applications, including as flame-retardants, UV stabilizers, and anti-microbial agents in polymer nanocomposites as well as a photo-absorber in a solar cell. Here an overview of LDH synthesis and modification, composite preparation as well as characterization is given to highlight the unique ability for customization of LDH.

KEYWORDS

layered double hydroxide, polymer nanocomposites, rubber composites

1 | INTRODUCTION

Layered double hydroxides (LDHs), shown in Figure 1, are anionic layered clays consisting of trivalent (M^{III}) and divalent (M^{II}) metal cations that form a positively charged metal hydroxide layer which is balanced by an interlayer consisting of anions. The hydroxide layers of LDHs are similar to that of the mineral brucite ($Mg(OH)_2$) where some M^{II} ions are substituted by a M^{III} cation. LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{q-}_{x/q}\cdot nH_2O]$, where A is an anion with valency q. Further, x is the molar fraction of trivalent cations to total metal cations ($x = M^{III}/(M^{III} + M^{II})$) in the layer structure and is typically limited to $0.1 \leq x \leq 0.33$.

LDHs are easy to synthesize and customize. They can therefore be tailored for specific applications in nanocomposites depending on their hydroxide layer metal ion composition, synthesis method, and of course interlayer anion modification. This tuneability of LDH properties has led to a great interest in their use as functional fillers in polymer composites for many applications, and the use of layered materials to produce nanocomposites with improved mechanical, thermal, gas barrier properties is well established.

In this review, the synthesis, modification and use of LDHs to prepare polymer nanocomposites with specific applications that were investigated at Leibniz-Institut für Polymerforschung Dresden are considered in order to highlight 15 years of collaborative research with international partners. Recent developments in LDH synthesis are outlined, with a focus on more environmentally friendly and sustainable methods. Several LDH interlayer modification techniques are described and compared. The preparation of different polymer/LDH nanocomposites are discussed, and the common properties of such

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Dedicated to Prof Udo Wagenknecht, who hosted the first IPF colleague working on LDH: Francis Reny Costa.

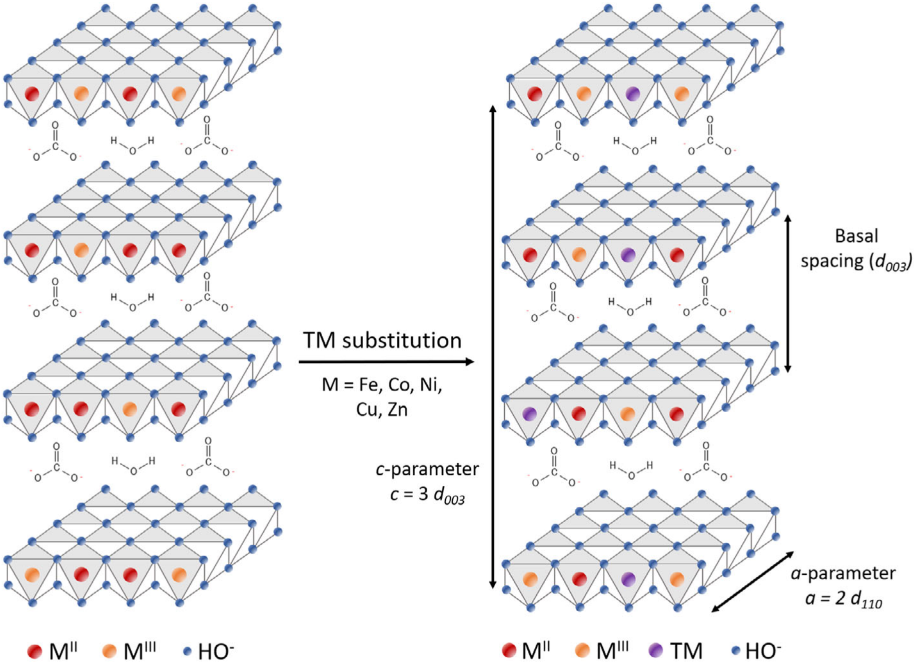

FIGURE 1 Schematic representation of a transition metal (TM) substitution where some metal cations of a di-metal M^{II}-M^{III} layered double hydroxide (LDH) with interlayer carbonate is substituted with a TM to from a tri-metal M^{II}-TM-M^{III} LDH with TM = Fe, Co, Ni, Cu, Zn.

hybrid materials are reported. Aside from the typical effects that LDHs have on nanocomposite morphology, rheology and mechanical properties, the improvement of functional properties like flame retardancy, UV stability and anti-oxidant behaviors of LDH based nanocomposites are reviewed in detail. Several specialty applications of LDH, such as in solar cells or anti-microbial fibers, are also considered to convey the potential applications of LDH based nanocomposites due to the ability to manipulate LDH properties through interlayer anion design.

2 | LDH SYNTHESIS

Several established synthesis methods exist, such as co-precipitation, urea hydrolysis, anion exchange, reconstruction, sol–gel synthesis, and the fast nucleation process. Co-precipitation is used most often, and in this method LDHs are synthesized using a mixed metal salt solution (typically metal chlorides, nitrates, or sulfates) and a base solution (usually NaOH or KOH). Both are added dropwise to a beaker that contains the anion to be intercalated. The LDH then precipitates out of the solution. Carbonate contamination of the interlayer often occurs when the synthesis by this method is not done in an inert environment and with decarbonated water. This is due to the high affinity of the LDH interlayer for carbonate anions. It is a very simple technique that can be tailored to prepare LDHs from a large array of different metal cations and interlayer anions. It is also a very polluting synthesis method, as it results in large amounts of salt-rich wastewater that needs treatment. Further, if highly crystalline and/or large LDH particles are desired, then the LDH material produced via co-precipitation requires hydrothermal treatment. Another popular synthesis technique is the urea hydrolysis method. In this method, urea is used to develop the base to precipitate LDH out of the metal salts solution through homogenous nucleation. Temperature is used to control the urea hydrolysis rate and therefore the pH of the solution. This method leads to the formation of large, well-crystallized LDH platelets and reduces the need of excessive LDH washing that is required in the co-precipitation method. Several works have suggested that Al hydroxides could form during the initial stages of homogeneous precipitation, which then act as LDH seeds or nucleation points.[1,2] As the hydrolysis progresses further and the pH increases further, the previously precipitated $Al(OH)_3$ can dissolve and be incorporated together with divalent cations into LDH hydroxide layers.[1] However, this could lead to some $Al(OH)_3$ in the final LDH product.

Since the synthesis method, specific conditions and post-treatment all influence the material properties of LDH, a comparison of LDH materials is difficult. Gevers[3] and Naseem[4] prepared several Mg-Al LDHs substituted with different transition metals (TMs) under the same conditions to determine the effect that the TM substitutions have on the LDH material properties. A schematic representation of the substitution of a TM is shown below in Figure 1. Since the same LDHs were prepared in these works, they can be used to compare the effect the synthesis methods, namely co-precipitation and urea hydrolysis, have on the resultant LDHs.

Gevers[3] synthesized TM Mg-M-Al LDHs (M = Fe, Co, Ni, Cu, Zn) using constant pH co-precipitation with

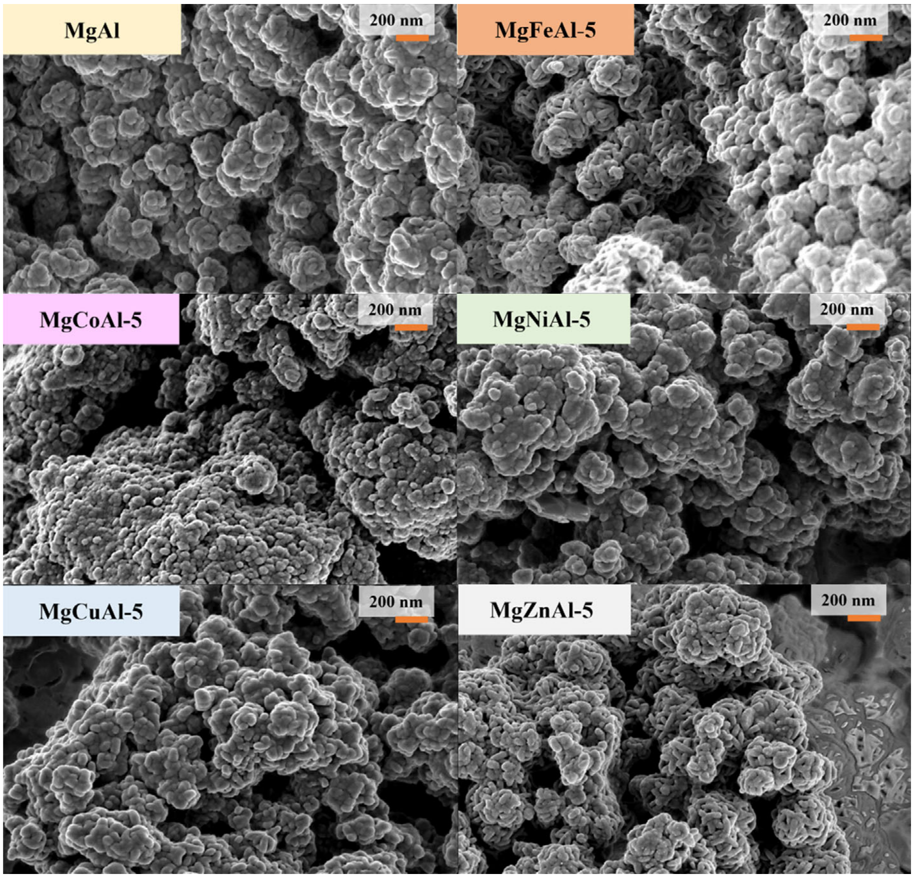

FIGURE 2 Scanning electron microscope (SEM) images of the transition metal (TM)-substituted Mg-M-Al layered double hydroxides (LDHs) synthesized via co-precipitation. Reproduced with permission.[3] 2019, RSC Publishing.

substitutions of 0.5, 1, 5, 10, and 25 mol% based on Mg replacement for divalent TM cations and Al replacement for trivalent TM cations. The synthesis conditions used led to the successful preparation of all the desired LDHs, other than the cobalt substituted LDHs, with great purity. It is not clear whether a separate Co-phase was formed or if a partially oxidized Mg-Co^{II+}-Co^{III+}-Al LDH was formed. All the prepared LDHs had XRD spectra as expected for the rhombohedral $R\overline{3}m$ structure, with clear reflections, although some broadening indicated that only small crystallites formed. The TM used, as well as the degree of the substitution, influenced the a and c crystal parameters. The a-parameter was independent of the interlayer composition and could be used to determine if the layer composition modification was successful. In this work, the increase in a for M = Fe, Cu, Zn as well as the decrease of a at higher Ni substitutions corresponds well to the atomic radii of the VI coordinated cations in the crystal lattice. The c-parameter is a function of the cation radius of the metals in the hydroxide layer, as well as the number of water molecules and orientation of the anions within the interlayer. The differences were consistent with the varying amount of interlayer water in the LDHs as determined by thermogravimetric analysis (TGA). The LDHs all had a similar morphology as shown in Figure 2: globular assemblies of nano-sized platelets, which is usual for unaged, co-precipitated LDHs. The platelet sizes varied depending on the TM used as well as the amount of TM substitution. The calculated crystallite sizes from X-ray diffraction (XRD) data using the Scherrer equation correlated extremely well to the observations from scanning electron microscope (SEM) regarding the changes in platelet size. Crystallite thickness increased with an increase in TM substitution (except for a 10 mol% Ni substitution) and followed the general trend Mg-Ni-Al ≈ Mg-Zn-Al < Mg-Cu-Al ≈ Mg-Fe-Al < Mg-Co-Al LDH. In addition to the difference in interlayer water, TGA analysis showed that TM substitution had an effect on the two decomposition steps of the hydroxide layers (dehydroxylation and decarbonation: first a loss of Al-bound OH$^-$, then a loss of Mg-bound OH$^-$ and CO$_3^{2-}$). Overall, stability followed the trend Mg-Cu-Al < Mg-Zn-Al < Mg-Co-Al < Mg-Al < Mg-Ni-Al ≈ Mg-Fe-Al LDH. Mass loss decreased with an increase in TM substitution for Cu-, Zn-, and Co-substituted LDHs. The mass loss remained similar for the Fe-substituted LDHs and increased with an increase in Ni-substitution.

Naseem[4] prepared the same Mg-M-Al LDHs as in the previous work by the urea hydrolysis method and compared their properties. Substitutions of 5 and 10 mol% were performed. In all cases well defined, large platelet LDH crystals with the typical hexagonal platelet structure

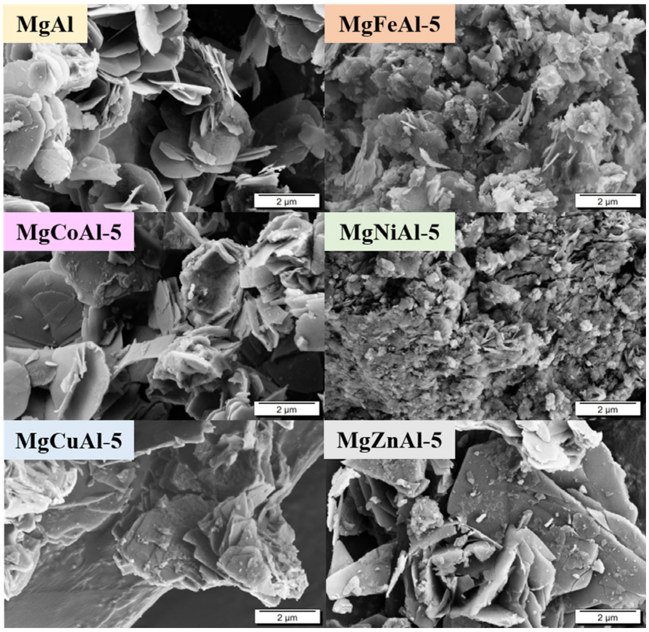

FIGURE 3 Scanning electron microscope (SEM) images of Mg-Al layered double hydroxide (LDH) and Mg-M-Al LDH with M = Fe, Co, Ni, Cu, Zn synthesized via the urea hydrolysis. Reproduced with permission.[4] 2019, RSC Publishing.

were prepared. The *a* crystal parameter increased with 5 mol% substitutions of all the TMs. Changes in *c* were likely due to changes in interstitial water content or anion orientation/ordering. The crystallite thickness increased when Co, Cu, and Zn substitutions were used but decreased when Fe and Ni were substituted into the hydroxide layer. This is different to when co-precipitation was used, where all TM substitutions increased the crystal thickness. Both platelet diameter and crystallite thickness correlated well with atomic radii of the TMs as well as each other. Unlike when co-precipitation was used, the TM substitution had a notable effect on the morphology of the prepared LDHs as can be seen in the SEM images in Figure 3. Larger, more well-defined hexagonal platelets were also prepared than when co-precipitation was used. Overall, TMs were well distributed throughout the LDH layers at 5 mol% substitution. Local variations in cobalt distribution is likely due to a layered α-Co(OH)$_2$ side-species that formed. The thermal properties of the Mg-Al LDH were also influenced by the TM substitutions. An increase in TM content led to an increase in stability for Ni-substituted LDH and a decrease in stability for Cu- and Zn-substituted LDH with respect to the lower-substituted LDHs. The residual weight after decomposition increased with TM substitution and was higher at 10 mol% substitution. The observed thermal stability took the order MgNiAl → MgFeAl = MgAl → MgCoAl → MgCuAl → MgZnAl-LDH. The urea hydrolysis proved to be a simple preparation method for well-defined crystallite structures with large hexagonal platelets and good distribution of TM atoms in the substituted LDHs.

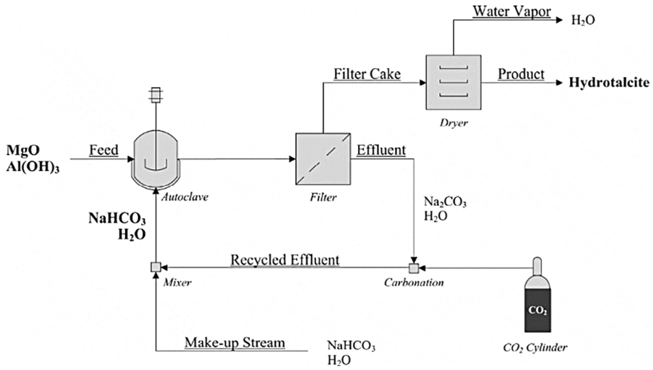

FIGURE 4 Block diagram of effluent free hydrotalcite production showing recycle routes and processing steps required as taken from. Reproduced with permission.[5] 2018, Taylor & Francis Group.

In addition to co-precipitation and urea hydrolysis, sol–gel synthesis is also often used. Despite attempts to make the sol–gel synthesis more sustainable, all three of these methods remain unfriendly to the environment. Less frequently used methods, like hydrothermal or mechanochemical synthesis, were developed to be more environmentally friendly procedures. In the hydrothermal synthesis route metal oxides and/or hydroxides are used in a dissolution-precipitation reaction to prepare LDHs. This synthesis method eliminates the harsh salt-containing effluent that is a product of both the urea and co-precipitation methods, which makes it a sustainable alternative. Unfortunately, the low solubility of metal oxides/hydroxides limits this synthesis method to a small window of favorable conditions at which quality LDH can be prepared. Labuschagné[5] describes a laboratory scale green synthesis process of hydrotalcite that is based on a patented industrial process developed by the same author(s). Hydrotalcite is a naturally occurring LDH form with the formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. The green synthesis method prepares Mg-Al LDH with a Mg:Al molar ratio of 2:1. A schematic of the synthesis procedure is shown in Figure 4. Sodium bicarbonate ($NaHCO_3$) is regenerated by bubbling through the sodium carbonate (Na_2CO_3) effluent before being fed to the reactor during the next run. This eliminates the need for salt effluent treatment and lowers the amount of sodium carbonate needed to be fed fresh for each run. The synthesis method relies on the reaction of insoluble or low solubility metal oxides, hydroxides, or carbonates, which occurs through a dissociation–deposition–diffusion mechanism, sometimes noted as transport reaction. MgO dissolves and reacts with water before precipitating as brucite, which forms the basis for the LDH material. $Al(OH)_3$ dissolves to produce Al ions that replace of some of the magnesium ions in the brucite layers, producing the positively charged metal hydroxide layers of the LDH structure. Carbonate (CO_3^{2-}) anions are intercalated between the layers to balance the positive charge, which causes the LDH to precipitate out of solution. Higher reaction temperatures favor the formation of LDH. In fact, reacting at 180 °C for 5 h yields a 99.37% conversion of the reactants to MgAl-CO_3 LDH. The synthetic hydrotalcite had high crystallinity, large platelet size and morphological homogeneity—indicating the good quality of the product.

Following the green synthesis of Mg-Al LDH, a green synthesis procedure for the preparation of hydrocalumite was developed and described.[6] Again a hydrothermal synthesis route was followed, using a dissolution/precipitation reaction of $Ca(OH)_2$ and $Al(OH)_3$ in water. A bench top reactor with an inert nitrogen environment at a slight pressure was used. Under all the tested reaction conditions the formation of hydrocalumite was favored and between 50% and 85% of the final crystalline phases was Ca-Al LDH. The remaining phases mostly consisted of katoite. In fact, 84.91% Ca-Al LDH could be prepared under mild synthesis conditions (atmospheric pressure, temperatures less than boiling point, 3 h reaction time) using this setup. A low water-to-solids ratio, longer reaction times, good mixing, adequately high reaction temperatures, and the use of amorphous $Al(OH)_3$ with a high surface area in a calcium-to-aluminum ratio that stoichiometrically favors katoite formation all promoted hydrotalcite formation. Increasing the temperature to a high level led to $CaCO_3$ formation. Additionally, pH effects caused by the amount of reactants supplied could also have played a role in the increased purity observed, by increasing the dissolution of the $Al(OH)_3$ phase, especially for low water-to-solids ratios and the stoichiometrically unfavored molar calcium-to-aluminum ratios. Although conducted in an inert environment some carbonate contamination, from $Ca(OH)_2$ (as calcite) and from the surface adsorbed carbonate species on $Al(OH)_3$, could not be avoided.

In conclusion the choice of synthesis method must be determined by the final application of the LDH, since synthesis method strongly influences the platelet size, for example. Some methods are more difficult to use, if not even impossible, when metals other than Mg and Al are used. A selection of impressions can be found in Figure 5, where it is obvious, that co-precipitation results in rather small particles with diameters of about 20 nm, whereas urea hydrolysis tend to result in 1–2 μm particle diameters and the dissolution-precipitation mechanism leads to particle diameters as large as 20 μm. This would qualify the first for any catalytic application with a lot of accessible edges, whereas the last is better suited to, for example, barrier applications where a high aspect ratio is preferred.

3 | LDH MODIFICATION

Pristine LDH is not well suited for polymer composite preparation. The small interlayer spacing hinders polymer chain intercalation and the inorganic (hydrophilic) nature of LDH makes the additive incompatible with organic polymers. Typically, LDH is pre-treated by intercalating an organic anion species with a long hydrophobic tail, like sodium dodecylbenzenesulfonate (SDBS), shown in Figure 6. This increases the interlayer distance and makes the LDH more compatible with organic matrices, thereby aiding polymer intercalation and LDH exfoliation.

There are several methods to organically modify LDH structures in literature. This includes the in situ method, the ion exchange method, and the reconstruction method. The reconstruction method is based on a unique property of LDH material—the so-called structural memory effect. Most LDH clays can reconstruct their original structure after calcination by dispersing the oxides in an aqueous solution containing an anion. An advantage of this modification method is the lack of competing anions already present in the LDH. This method is particularly beneficial for the modification of CO_3^{2-} containing LDHs, as the high affinity of LDH for CO_3^{2-} prevents successful ion exchange.

Using the memory effect, also called reconstruction and sometimes the regeneration method, Mg-Al LDH can be successfully modified with SDBS, sodium laurate, sodium dodecylsulfate (SDS) and bis(2-ethylhexyl)phosphate (BEHP).[8] After reconstruction, the modified LDHs showed all the characteristic reflections corresponding to the original LDH. However, as seen in Figure 7, a broadening of the reflections was observed. This suggests that the crystal structure reappears, although with some loss of crystallinity. Similar results were found when Mg-Al LDH was intercalated with straight-chain primary alkyl sulfonates of different chain lengths.[9] Regardless of hydrocarbon chain length, all the alkyl sulfonates were efficiently intercalated, and the layered structure of the LDH was reconstructed. When comparing alkyl sulfonates of different alkyl chain lengths to carboxylic acids of various chain lengths (C6, C8, and C14) as well as SDBS, BEHP, and lauric acid (LA), wide-angle X-ray scattering (WAXS) spectra indicated that alkyl sulfonates were the most efficient anionic surfactants for the modification of LDH by this method, resulting in a homogeneous structure. However all other anionic surfactants could also be intercalated into the LDH structure.[10] As

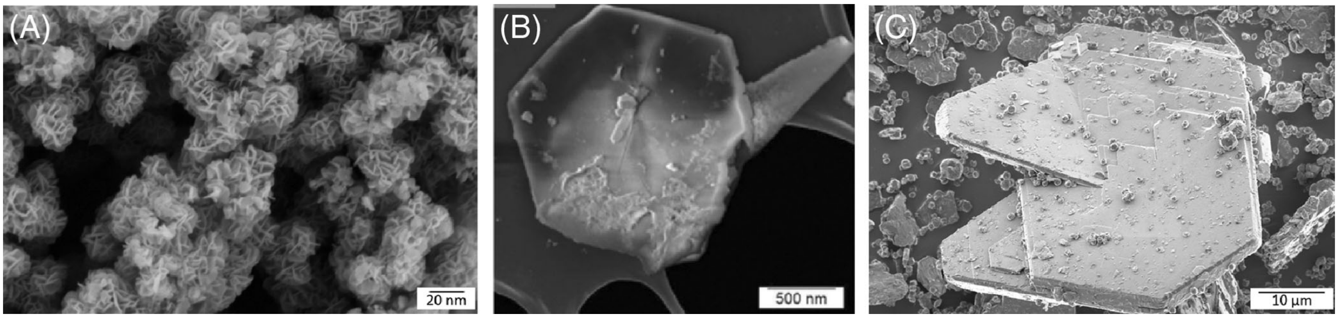

FIGURE 5 Typical particles derived from (A) co-precipitation, (B) urea hydrolysis (reproduced with permission[7] 2014, Elsevier) and (C) dissolution-precipitation synthesis methods.

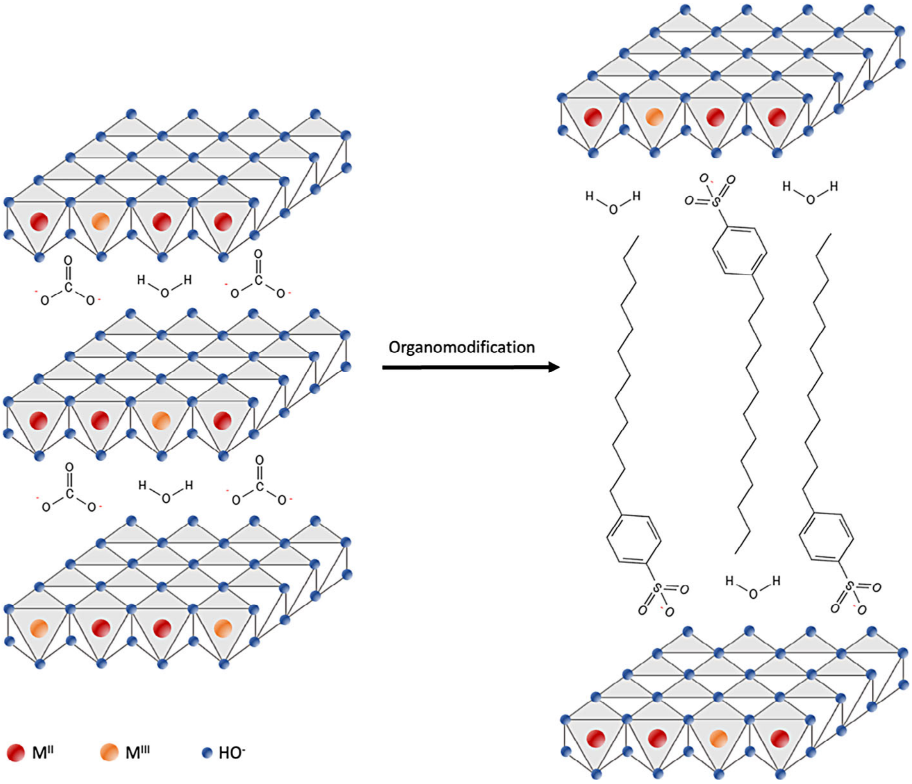

FIGURE 6 Typical layered double hydroxide (LDH) structure before and after organo-modification with sodium dodecylbenzenesulfonate (SDBS) via an anionic exchange reaction.

expected, the positions of the basal reflections of all modified samples are shifted to higher d values, showing the expansion in the interlayer distance.[8–10] A linear relationship between the basal spacing and the number of carbon atoms in the alkyl chain, for even numbered carboxylic chain lengths, existed.[9] This agrees with a monolayer arrangement of the alkyl sulfonates in the LDH interlayer where the chain is slightly tilted. Overall, the modified Mg-Al LDHs kept the plate-like structure of the unmodified LDH but the hexagonal shapes were irregular.[8,9] Figure 8 shows these irregularities of Mg-Al modified with SDBS, sodium laurate, SDS, and BEHP. The alkyl chain length had a significant influence on the particle morphology. C6 and C8 lengths gave rise to a honeycomb-like structure due to secondary growth of the crystallites in the transverse direction on primary particles. When alkyl sulfonates with chain lengths C10–C14 were intercalated into the LDH, primary particles aggregated to form a house-of-cards-like structure.[9] Therefore, the increase in particle thickness was more than expected from an increase in interlayer distance.

Typically, inorganic LDHs undergo two-stage thermal decomposition. First, roughly up to 200 °C, physically absorbed and interlayer water is lost. At higher temperatures (225–500 °C) decomposition of the LDH structure due to the loss of interlayer carbonate and dehydroxylation of the metal hydroxide layer occurs.[11–14] When Mg-Al LDHs with Mg^{2+}/Al^{3+} ratios of 2 or more decompose, the LDH decomposition step is split into two distinct stages. The loss of water is followed first by the partial

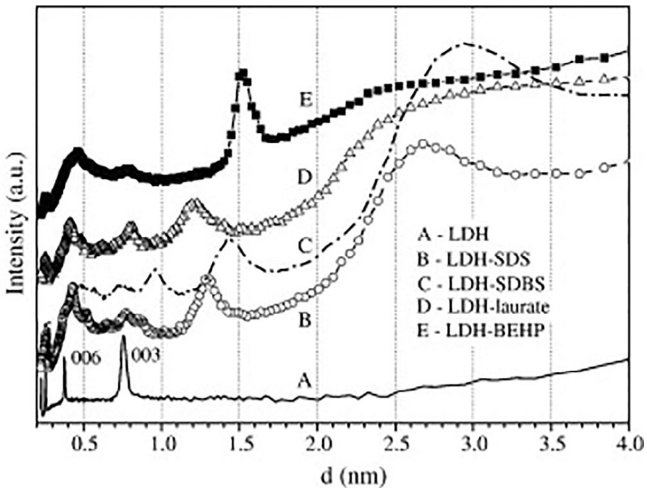

FIGURE 7 X-ray diffraction (XRD) diagram of modified layered double hydroxide (LDH) obtained by reconstruction in presence of various surfactants. Reproduced with permission.[8] 2008, Elsevier.

loss of OH$^-$ from the hydroxide layer, and then complete dehydroxylation and loss of interlayer carbonate.[11–14] The modified Mg-Al LDHs still showed three main decomposition steps but at different temperatures.[8,9] The loss of absorbed and interlayer water occurred at much lower temperatures[8,9] due to the weaker interactions between the water and intercalated organic anions. However, the decomposition, which includes dehydroxylation of the hydroxide layers as well as the decomposition and loss of the interlayer anions, of organo-modified LDHs occurred at higher temperatures.[8,9] The thermal decomposition is dependent on the intercalated anions, for example, an increase in hydrocarbon tail size led to a decrease the stability of the sulfonate.[9]

In addition to modification of LDH structures to increase polymer compatibility, these structures can also be used as hosts for organic molecules that offer specific active properties. The LDH structure ensures stability during processing while the active intercalated species can provide a composite with an added property. Of course, the organic nature of the intercalated ion will also improve LDH/matrix compatibility and increase the interlayer distance, which will improve LDH dispersion and distribution. For example, the sterically hindered phenol-type antioxidant, 3-(3, 5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid (BHPPA) was intercalated into a Mg-Al LDH via reconstruction.[15] Consistent with other modification studies, the interlayer spacing of the reconstructed Mg-Al BHPPA LDH increased significantly with the intercalation of the large anion. XRD patterns also showed a slight broadening of each reflection, which could indicate a loss of crystallinity or turbostratic disorder. Overall, the hexagonal platelet morphology of the LDH was retained after modification. Further, the thermal stability of BHPPA was increased by almost 100 °C after intercalation into the LDH structure. Most importantly, BHPPA retained its radical scavenging ability and exhibited sustained antioxidant activity after intercalation. This means that intercalation of active antioxidants into LDH galleries is a good strategy to enhance their stability and longevity.

In some situations, anion exchange is preferred. However, as the carbonate anion is difficult to replace, a decarbonisation pre-treatment step with solutions, like HCl–NaCl, ammonium salt alcohol, or acetate buffer/NaCl, is necessary before the anion exchange reaction. Jaerger and coworkers[16] modified green Ni-Al LDH and pink Co-Al LDH prepared with urea hydrolysis with SDS, sodium laurate, sodium palmitate, and sodium stearate via anion exchange after decarbonation. In an acetate buffer solution containing NaCl the CO_3^{2-} ions are typically replaced with chloride ions. These pretreatment procedures are complicated and only reported for very small sample sizes. Thus, a one-pot anion-exchange intercalation procedure, where CO_3^{2-} is first replaced by NO_3^-, followed by a surfactant/NO_3^- exchange, was developed.[7] The LDH was prepared using urea hydrolysis and the synthesis conditions affected the success of the subsequent LDH modification via the novel one-pot method. Not only did the urea proportions (k, where $k = [\text{urea}]/([\text{Mg}] + [\text{Al}])$), determine crystalline LDH formation, but also the modification afterwards. The optimum urea content for the LDH synthesis and modification was $k = 3$. The platelet size, and thus synthesis time, of the unmodified LDH also affected the one-pot anion exchange. The anion exchange of short and bulky anions favored smaller LDH platelets. When compared to other modification methods, the new one-pot anion exchange was more suited for smaller anions, while reconstruction preformed the best when intercalating larger molecules. Therefore, the modification method should be selected based on the size of the selected intercalation molecule.

The biggest drawback of reconstruction is the large amount of energy that is necessary for the calcination of the LDH. Further, changes in the crystallinity and composition occur after reconstruction.[17] In situ synthesis of polymer nanocomposites is a not very efficient intercalation method under ambient conditions due to the interference of CO_3^{2-}, which has a strong affinity for LDH layers. In the case of in situ synthesis of polymer composites via co-precipitation, scale up and use in polyolefin systems are still problematic. Therefore, Wang[18] developed a one-step synthesis method for the preparation of organic anion

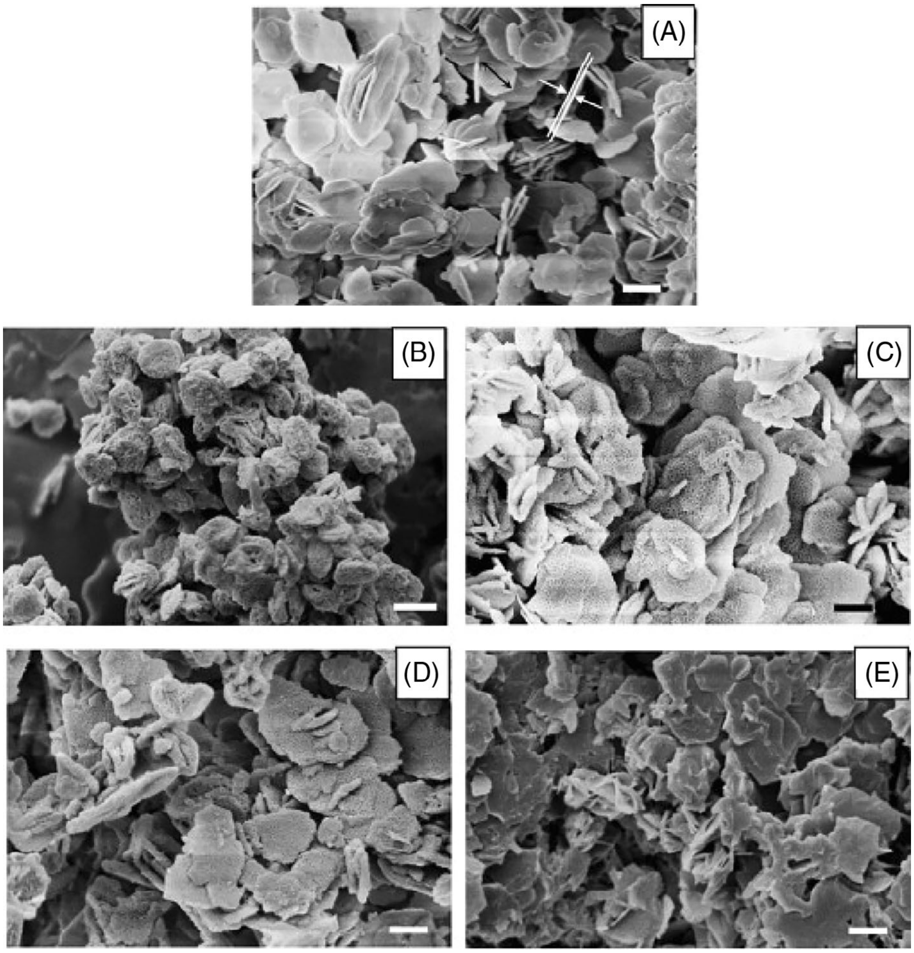

FIGURE 8 Scanning electron microscope (SEM) micrographs of: unmodified layered double hydroxide (LDH) and LDH modified with (B) laurate (C) sodium dodecylsulfate (SDS), (D) sodium dodecylbenzenesulfonate (SDBS), and (E) bis(2-ethylhexyl)phosphate (BEHP). The magnification bar indicates 2 μm length. Reproduced with permission.[8] 2008, Elsevier.

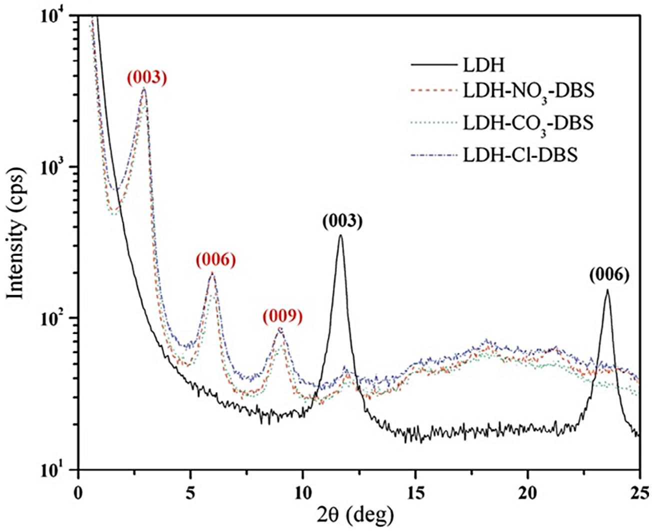

FIGURE 9 Wide-angle X-ray scattering (WAXS) patterns for pure layered double hydroxide (LDH) and LDH modified by one-step synthesis. Reproduced with permission.[18] 2009, American Chemical Society.

intercalated LDHs. In this method co-precipitation in the presence of organic species, under ambient conditions, is used. It is worth noting that the "carbonate-free condition" is not required but the pH control is critical to eliminate/minimize carbonate intercalation.

SDBS could be efficiently intercalated into Mg-Al LDH with the one-step method.[18] Moreover, the WAXS patterns of the organic LDHs, shown in Figure 9, prepared in the presence of different starting anions (Cl^-, NO_3^-, and CO_3^{2-}) show the same final interlayer distances, demonstrating the efficiency of the one-step method regardless of the metal salts used as starting material.[18] The modified Mg-Al SDBS LDHs had a high degree of crystallinity and homogeneity in composition. Following the work on commonly studied Mg-Al LDH, Co-Al LDH intercalated with SDBS was prepared by this method.[19] The WAXS pattern of the organic Co-Al DBS LDH and calculation by the Bragg equation show that the interlayer distance (d) value is enlarged from 0.75 to 3.10 nm. Thus, self-assembling was successful. The absence of any distinguishable reflection (003) at $2\theta = 11.8°$ for both the Mg-Al SBDS and Co-Al SDBS LDHs suggest that no inorganic LDH was formed.[18,19] All the organic LDHs consisted of plate-like particles with irregular and undefined shapes,[18,19] as shown in SEM images in Figure 10. This could be due to the presence of the modifier, not only in the interlayer but also on the surface of the LDH.[19] It is worth noting that

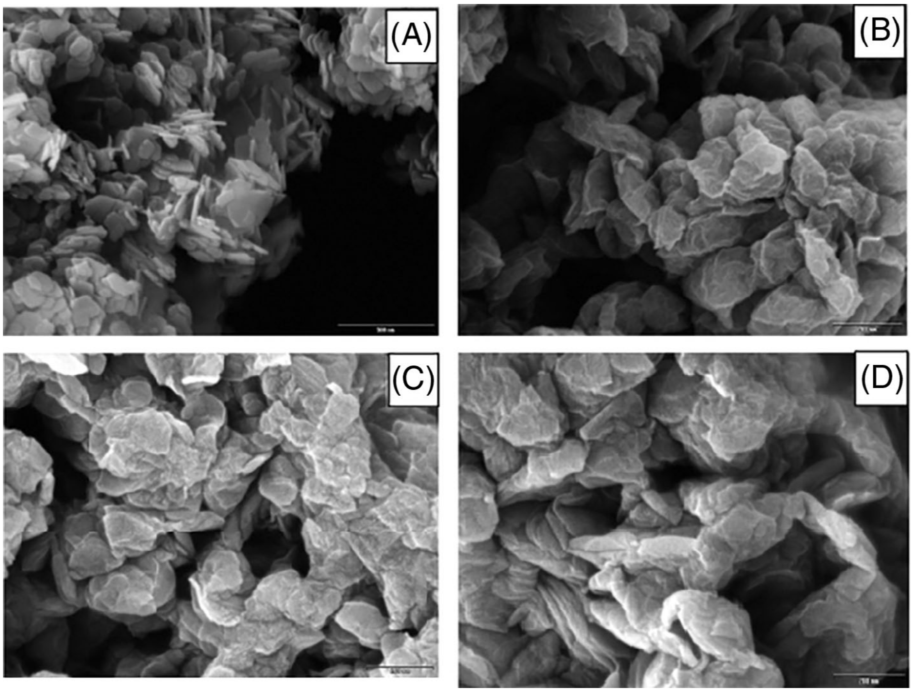

FIGURE 10 Scanning electron microscope (SEM) micrographs showing the particle morphology of the layered double hydroxide (LDH) samples obtained by one-step synthesis: (A) Mg-Al LDH (CO_3), (B) Mg-Al sodium dodecylbenzenesulfonate (SDBS) LDH (CL), (C) Mg-Al SDBS LDH (CO_3), and (D) Mg-Al SDBS LDH (NO_3). Reproduced with permission.[18] 2009, American Chemical Society.

CO_3^{2-} contamination in the interlayer could not be avoided completely, but was only at a low level when compared to other methods.[18]

Following the success of these earlier works, the one-step synthesis method was subsequently used to synthesize not only binary Mg-Al LDH, but also ternary Mg-Zn-Al LDH modified with SDBS.[20] Other anions like acid yellow 36 (AY36) and acid red 88 (AR88) were also intercalated into Mg-Al LDH in this way.[21]

As shown above, LDHs can be synthesized using many different techniques and their properties can be tailored to suit many different applications. For this reason, LDHs can be used in various types of polymers to fulfill different roles. A discussion of the variety of LDH applications in polymers follows.

4 | LDHs IN THERMOPLASTIC POLYMER COMPOSITES

The use of natural and synthetic layered fillers to prepare polymer nanocomposites (PNCs) and polymer micro composites can improve several polymer properties, especially mechanical-, gas barrier-, and flame retardancy properties. PNCs are materials in which the polymer matrix is filled with particles that have at least one dimension in the nanometer range, normally smaller than 100 nm. Layered compounds such as LDHs are composed of 2D layers of which at least one can be in the nanosized range, even more so after partial exfoliation of LDH platelets or polymer intercalation during processing. This makes LDH an ideal filler for creating PNCs. In recent years, LDHs have been increasingly studied as nanofillers for polymer composites. In addition to the plate-like nature of LDH, it has several advantages over other layered nanofillers such as silicates. This includes the large variety of inorganic and organic anion species that can be intercalated into an LDH. The metal hydroxide (like $Mg(OH)_2$ and $Al(OH)_3$) type thermal decomposition behavior as well as the simple synthesis procedure and the homogenous composition also make LDHs favorable from a processing perspective.

There are several processing techniques that can be used to prepare LDH/polymer nanocomposites. Most of these methods involve the intercalation of polymer chains into the interlayer of the LDH structure. In situ polymerization and direct intercalation in polymer solution are two such methods. Melt-intercalation or partial platelet exfoliation via melt mixing of a polymer with (usually an organically modified) LDH offers several advantages, most notably the ease of processing with commonly used equipment.

As is the case in all filled materials, the addition of LDHs to polymers affects the properties of the final composites, such as morphology, rheology, thermal stability, crystallization and mechanical properties. A discussion about these effects follows below.

4.1 | Effect of LDH on composite properties

4.1.1 | Morphology

The morphology of LDH PNCs can vary from well distributed, exfoliated platelets to large particle agglomerates present in localized domains, or a mixture of partially exfoliated particles, intercalated polymer chains and some undispersed tactoids. The morphology has a profound impact on the material properties and is thus important to determine in PNCs. Typical analysis of LDH/polymer composites includes XRD and WAXS in combination with electron microscopy. WAXS and XRD analysis can be used to describe the extent of intercalation and give an impression of possible exfoliation of the layered nanofiller in the polymer matrix. Complete (or high degree of) exfoliation leads to the disappearance of corresponding reflections from the XRD spectra of the composites. However, other factors can cause the disappearance of reflections from the XRD spectra. Transmission electron microscopy (TEM) and SEM images are therefore also necessary to support the XRD and WAXS results and to study the dispersion, as well as the degree of platelet exfoliation and polymer intercalation of the LDH particles in the polymer matrix.

In composites prepared with unmodified Mg-Al LDH, the LDH was present as large tactoids, as the LDH layers were not intercalated nor the platelets exfoliated.[22] After modification with BHPPA, the XRD spectra of the resultant composites showed a shift and broadening of the characteristic crystalline basal reflection, which suggest that the LDH particles were intercalated with polymer chains and/or partially exfoliated. This was confirmed with TEM images, which showed the LDH layers were well dispersed and intercalated throughout the polypropylene (PP) matrix with a high degree platelet delamination.[22]

The LDH modifier also plays a role. An increase in the size of the organic modifier increases the interlayer distance of the LDH, which in turn eases the intercalation of polymer chains and exfoliation of the LDH platelets during processing.[10] A critical chain length of the organic modifier, and thus the interlayer distance of the organo-modified LDH, exists at which the particle morphology changes from dominated by non-intercalated and large LDH tactoids to a state with highly exfoliated LDH particles in the nanocomposite, as shown in Figure 11.[10] Further, the functional groups of the modifier also affect PNC morphology. Despite the better modification of LDH by alkylsulfonates, carboxylate modified LDHs were more easily dispersed and exfoliated in polyolefin matrix during melt compounding. This could be due to the similar natures of carboxylate and MAH-g-PE, enhancing polymer intercalation in the clay structure.[10] After compounding poly(ϵ-caprolactone) (PCL) with Mg-Al LDH modified with stearic acid and SDBS, the resultant XRD spectra showed no significant changes in the reflections of the organo-modified LDHs. However, higher order peaks became weaker or even disappeared. This suggested that complete LDH exfoliation was not achieved and that the LDH crystal structure was still mostly intact. TEM images showed DBS modified Mg-Al LDH was distributed more uniformly throughout the PCL matrix, although the stearate modified LDH was better distributed at the nanoscale. A mixed morphology of individually dispersed particles and some tactoids was achieved for both organo-modified LDH nanocomposites.

4.1.2 | Rheology

Rheological analyses investigate the linear viscoelastic properties of nanocomposites. It can provide useful insights into the nature and degree of particle dispersion in a polymer matrix. The melt rheology of polymer nanocomposites differs from the pure polymers due to the microscopic and mesoscopic structures of the clay particles and their interaction with the polymer matrix and each other. In the linear viscoelastic regime, when a low shear rate and frequency is used, the rheological behavior of a composite is very sensitive to any change in its microstructure. This provides information on the clay particle distribution, and particle–particle and particle–polymer interactions. The particle–particle interactions are attractive and can cause the formation of localized domains of clay particles where the structural units remain physically correlated. The evolution of such a filler network structure could be investigated by non-linear shear experiments.

With the addition of LDH, the viscosity of the composite increases, as is expected for filled polymer materials. At low LDH loadings, the change in viscosity is attributed to polymer–filler interactions. As the LDH loading increases, polymer-nanofiller networks develop. This marks a change in the composite's behavior from a liquid to solid-like due to the polymer–filler as well as filler–filler interactions.[23] The pseudo solid-state behavior at high LDH loadings is also seen in the temperature dependence of the rheological properties of the material. Above a certain LDH concentration, the nanocomposite melt behavior deviates from typical liquid-like-low-frequency flow behaviors and becomes independent of temperature.[24]

The linear viscoelastic response of the LDH nanocomposites is usually characterized in terms of storage modulus (G'), loss modulus (G'') and complex viscosity (η^*). G' describes the elasticity or stiffness of a material and is associated with the energy that is stored in the material. G' increases monotonically with increasing LDH loadings at low frequencies.[22–25] G'' measures the plastic component of a material and is related to the dispersion of energy. G'' has similar behavior to G', increasing monotonically with the concentration of LDH at low frequencies.[23] G' and G'' both increase as the frequency increases, but at higher

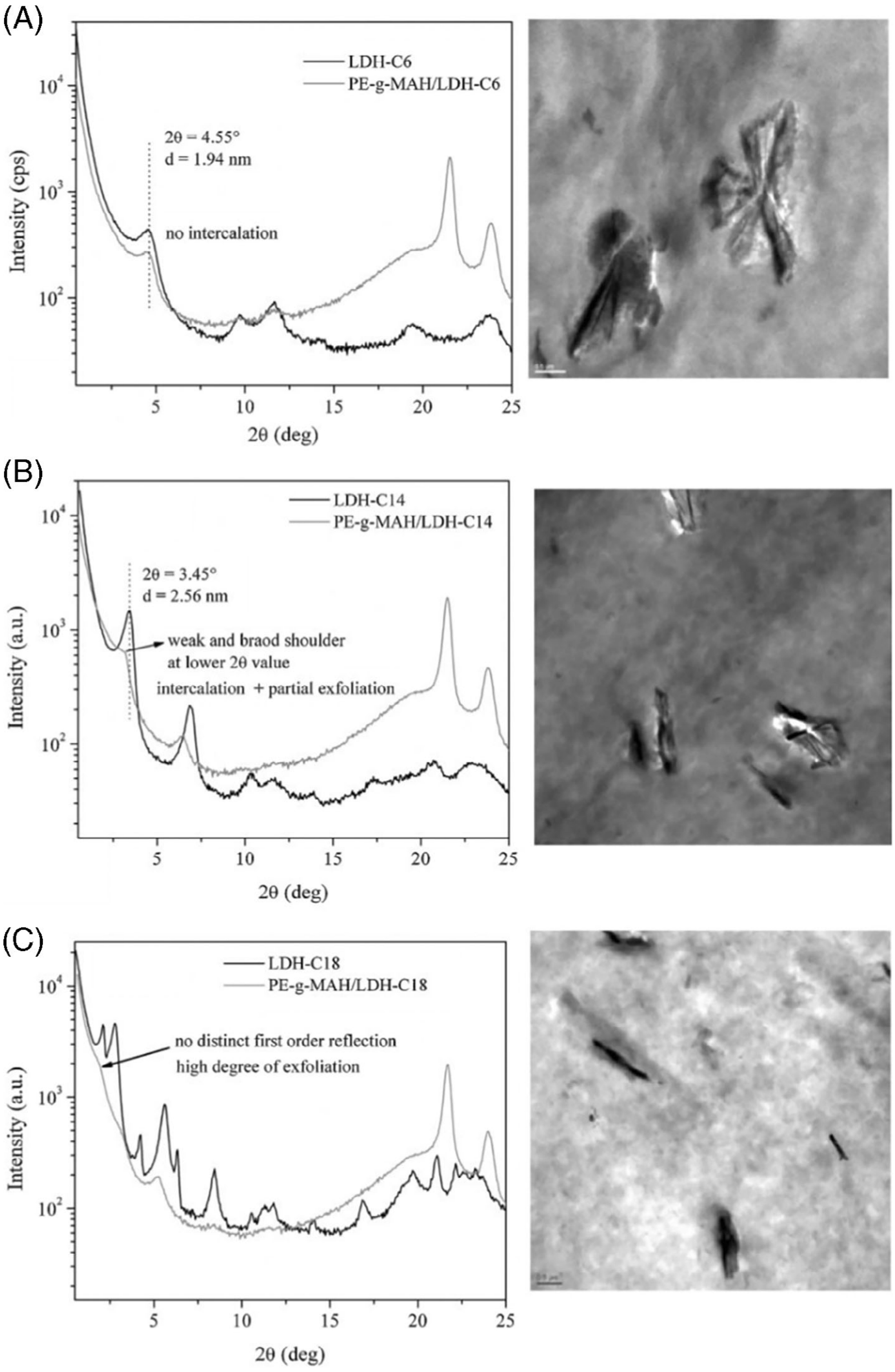

FIGURE 11 Morphological analysis of MAH-g-PE/organo-modified layered double hydroxide (LDH) nanocomposites containing 5 wt% LDH (left column: Wide-angle X-ray scattering (WAXS) patterns of organic LDHs and their corresponding polymer nanocomposites (PNCs), the right column: Transmission electron microscopy (TEM) micrographs of the nanocomposites, with a scale of 0.5 mm). LDH modified with (A) C6 alkylsulfonate, (B) C14 alkylsulfonate, and (C) C18 alkylsulfonate. Reproduced with permission.[10] 2011, John Wiley and Sons.

frequencies both become less dependent on the frequency and LDH content.[23] These behaviors are shown in Figure 12.

Polymer/LDH compatibility also influences the viscoelastic behavior of nanocomposites.[24,26] For Mg-Al SDBS LDH systems in maleic anhydride grafted high density polyethylene (MAH-g-HDPE) or maleic anhydride grafted polyethylene/low density polyethylene (MAH-g-PE/LDPE), the storage modulus increases with increasing LDH concentration. The change is much larger in the MAH-g-HDPE system, as is evident from Figure 12. This suggests that the polar matrix was more compatible with LDH than the nonpolar matrix, leading to better polymer/LDH interaction and particle distribution. XRD and TEM analysis suggested that the MAH-g-HDPE/Mg-Al SDBS LDH composites showed signs of partial LDH exfoliation, especially at low LDH loadings. In comparison the LDPE/MAH-g-PE/Mg-Al SDBS LDH composites morphology was complex and no exfoliation was observed.[24] Overall, LDH particle dispersion was better

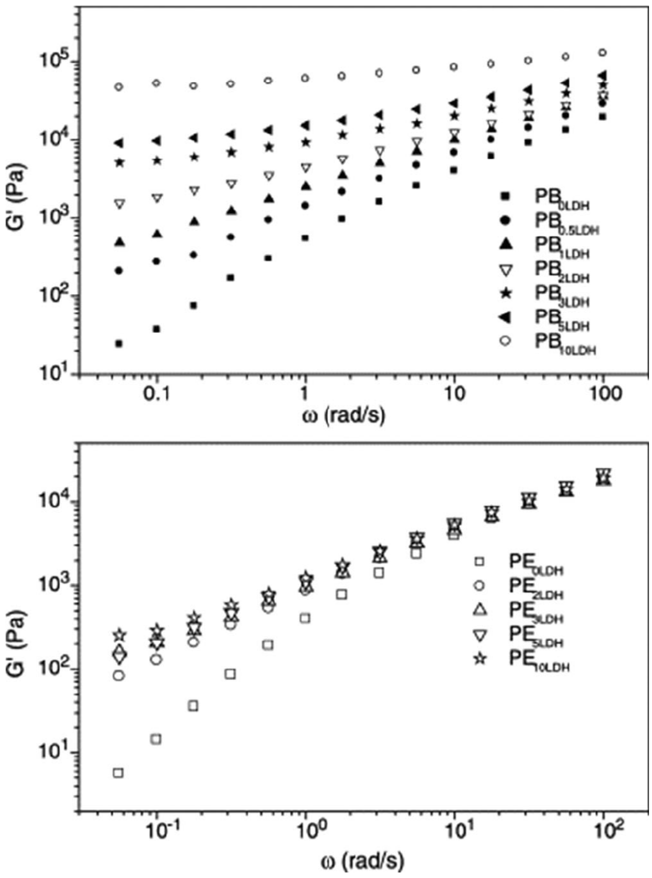

FIGURE 12 Effects of layered double hydroxide (LDH) loading on the temperature dependence of complex viscosity at low frequency (0.177 rad s^{-1}) of polyethylene/LDH nanocomposites. Reproduced with permission.[24] 2006, Elsevier.

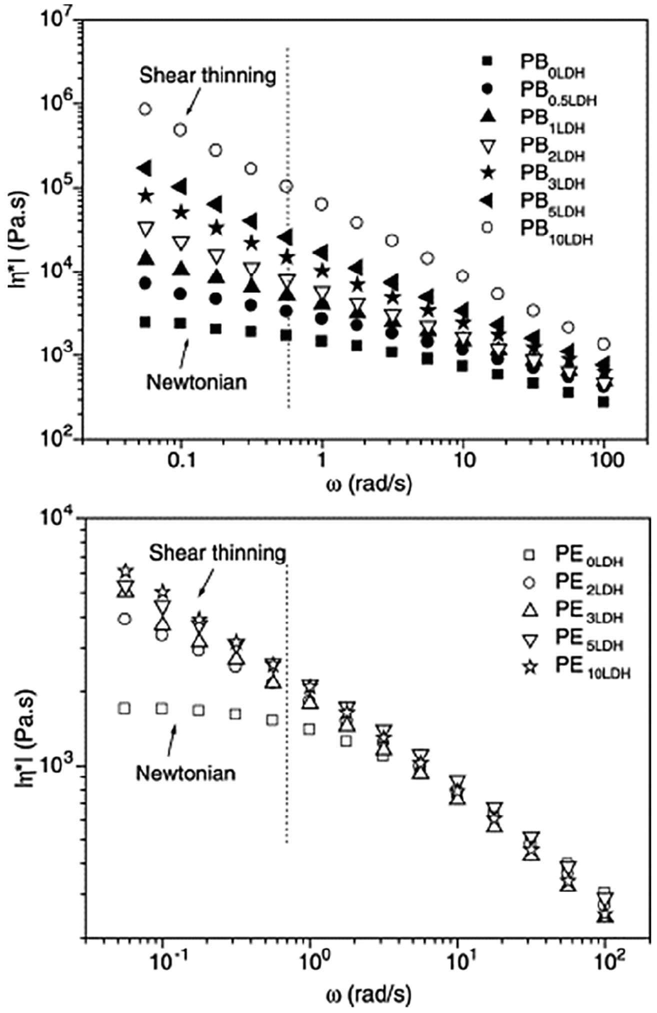

FIGURE 13 Complex viscosity ($|\eta^*|$) versus frequency (ω) curves (at 240 °C) for different nanocomposite samples showing the effects of layered double hydroxide (LDH) loading on flow behaviors in the low frequency regime. Reproduced with permission.[24] 2006, Elsevier.

in MAH-g-HDPE. In MAH-g-PE/LDPE compatibilizer particle rich regions restricted the homogenous distribution of LDH particles in the whole matrix.[24] Jaerger[26] reports an unexpected *decrease* in G' and G'' of LDPE/organo-modified Ni-Al LDH where no compatibilizer was used, due to a phase separation process. This LDPE-LDH phase separation was attributed to formation of aggregates that are segregated from the continuous phase of LDPE-LDH nanocomposites.[26]

Other factors, like the specific processing conditions, also influence the viscoelastic behavior of nanocomposites. For example, the effect of LDH on viscoelastic properties of the polymer is more noticeable when direct melt-compounding is used, where lower particle dispersion is generally achieved. This leads to increased filler–filler interaction when compared to other composite preparation techniques like sonication-assisted masterbatch melt mixing.[23] It is important to note that in a system with an added compatibilizer such as MAH-g-PE, which has a lower viscosity than the pure LDPE polymer, will also influence the viscoelastic behavior of the composite material. The decreased viscosities of Mg-Al and Mg-Fe-Al LDH/MAH-g-PP/PP composites are therefore attributed to the influence of the compatibilizer.[27] The decrease in viscosity was more prominent in Mg-Fe-Al LDH composites, likely due to a catalytic degradation effect that the Fe LDH had on the PP polymer and compatibilizer during processing.[27]

Characterization of a material's rheology often involves an analysis of its complex viscosity (η*) versus frequency (ω) plot as it is often more helpful to understand filler effects than absolute viscoelastic values. A shear-thinning exponent (n) can be used to quantify the transition of the melt behavior from liquid-like to a pseudo-solid-state.[24] This exponent is determined by fitting the low-frequency data on a logarithmic scale to a

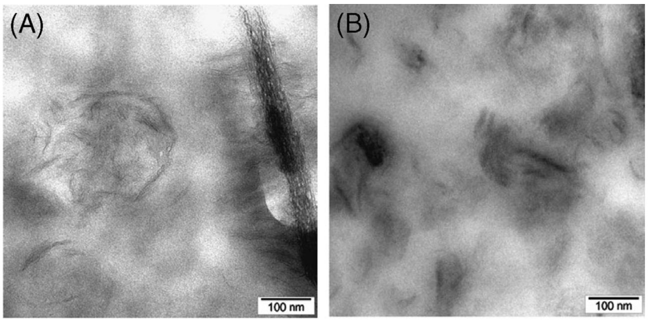

FIGURE 14 Transmission electron microscopy (TEM) micrographs of polyethylene/layered double hydroxide (PE/LDH) nanocomposites with (A) 5 wt% and (B) 10 wt% LDH loading, showing the partially exfoliated nature. The presence of intercalated tactoids is also apparent. Reproduced with permission.[29] 2006, Elsevier.

power law equation.[28] In a Newtonian liquid n is zero, as the negative value of n increases the shear-thinning nature of the material also increases. Alternatively, the relaxation exponent fitted by the logarithmic G' versus ω plot can also be used.

Unfilled polymer matrices show classical viscoelastic behavior, with Newtonian flow at low frequencies that transitions to shear thinning behavior at high frequencies.[24,25,29] LDH nanocomposites, however, have gradually increasing shear thinning behavior at low frequencies with increasing LDH loading, as shown in Figure 13.[10,24,25,29] At a certain LDH concentration, both the shear thinning and relaxation component becomes nearly independent of LDH loading.[24]

According to Wagner and Reisinger,[28] an increase in n indicates an increasing degree of particle exfoliation. Higher n values indicate higher degrees of exfoliation. However, at higher LDH concentrations the degree of exfoliation is not necessarily increased.[24,29] XRD and TEM analysis of Mg-Al SDBS LDH/MAH-g-PE/LDPE nanocomposites containing 5 and 10 wt% LDH showed the presence of both partially exfoliated platelets and intercalated plate-like LDH tactoids. Overall, the exfoliated platelets were well dispersed in the matrix. The tactoids formed domains with a physical network structure, which led to an inhomogeneous distribution of LDH particles throughout the matrix. Despite an increase in $|n|$ from 0.41 to 0.71 for 5 and 10 wt% LDH, particle exfoliation was not improved as shown in Figure 14.[29] The shear thinning behavior could instead have been caused by the inhibition of polymer chain relaxation due to more tethering of polymer chains on the particle surfaces, as well as a decrease in average distance between the dispersed platelets, which increases particle–particle interactions.[24,29]

As previously stated, the dispersed particles tend to form areas of oriented or physically correlated particles or polymer-nanofiller networks.[23,25,26,29] The network can either be present in localized domains or as a continuous network throughout the matrix.[25] This network effect increases at higher LDH concentrations due to the closer proximity of the particles, augmented by their attractive interaction.[24] These physically interconnected network structures were also observed by non-linear shearing experiments.[24]

Finally, it is worth noting that the LDH type and modifier both influence the PNC's rheology. The anion surfactant influences the interlayer distance of the modified LDH, and therefore the composite morphology and rheological behavior. Increasing d-spacing values resulted in increasing melt reinforcement. This is because, as the d-spacing increases, the ease of LDH exfoliation also increases, which in turn generates a higher number of exfoliated platelets per unit amount of the organo-modified LDH in the composite.[10]

4.1.3 | Mechanical properties

As expected, the addition of LDH to a polymer affects the mechanical properties of the nanocomposite. Usually the Young's modulus, or the stiffness of the composite, increases with an increase LDH loading.[20,29] This is likely due to the stiff nature of the platelets themselves. However, agglomeration of LDH particles can lead to a decrease in modulus at relatively high LDH loadings.[16] The elongation at break of polymers is lowered by LDH addition.[16,29] Jaerger[16] reported an anomalous increase in elongation at break of 300% when stearate modified Ni-Al LDH was used in LDPE at high LDH loadings. This could be due to the high affinity of the organic stearate anion for the polymer, coupled with the lubricating effect of stearate. The tensile strength (TS) of composites consisting of LDH/polymer and maleic anhydride compatibilizer, decreased.[20,29] The decrease in TS can be attributed to the MAH-g-PE (or MAH-g-PP) compatibilizer used in the composites.[29] In fact, at 15 wt% LDH, the TS increased when compared to a LDPE/ MAH-g-PE blend with similar compatibilizer loadings and no LDH. When considering LDPE composites with organo-modified green Ni-Al LDH and pink Co-Al LDH, the extruded nanocomposites, with loadings of up to 5 wt%, had similar Young's moduli and TSs compared to pure LDPE, although a decrease in these values was observed at 7 wt% LDH.[16]

To further understand the effect that LDH has on composite material properties, Costa[29] investigated the fracture behavior of Mg-Al SDBS LDH/MAH-g-PE/LDPE composites. The load displacement diagram indicated a ductile-to-brittle transition with increasing LDH content. The crack toughness behavior was studied based on the essential work of fracture (EWF) concept, where EWF is a measure of the resistance against crack initiation, and non-essential

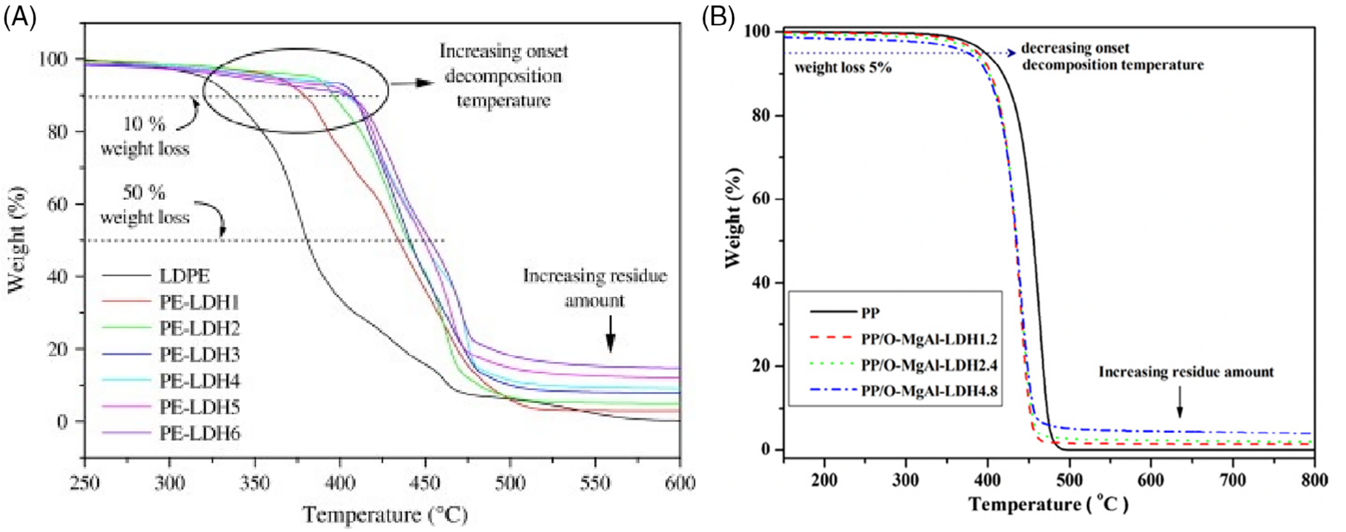

FIGURE 15 Thermogravimetric analysis (TGA) plots showing the decomposition behavior of nanocomposites of layered double hydroxide (LDH) modified with sodium dodecylbenzenesulfonate (SDBS) in (A) LDPE extruder where the sample is designated as PEXLDH, with X representing the wt% of LDH) (reproduced with permission[30] 2007, Elsevier) and (B) PP (reproduced with permission[33] 2011 Year, Elsevier).

work of fracture (βw_p) is a measure of the resistance against crack propagation. At up to 2.5 wt% LDH loading, crack initiation was primarily matrix-controlled. A large drop in EWF at 5 wt% LDH indicated a decreased resistance to crack initiation due to a transition in the nature of the material response with increasing LDH content. The non-linear dependence of βw_p on the content of LDH indicates a tough-to-brittle transition in these polymer nanocomposites. Both βw_p and the crack opening displacement (COD) had local maximum at 5 wt% LDH loading. Conceptually, COD is a measure of the inherent resistance of the material to stable crack propagation by crack blunting and is related to the size of outer plastic deformation zone in the post-yield fracture process zone.

4.1.4 | Thermal stability

The addition of LDH changes the thermal decomposition behavior of the polymer matrix. LDPE composites had higher initial decomposition temperatures and more residue remaining after decomposition when compared to pure LDPE, even at low LDH loadings, as shown in Figure 15.[30] These residues consisted of metal oxides and some carbonaceous material. When different LDHs were added to PP, a decrease in the initial thermal decomposition temperature was found.[20,31–33] This decrease was larger at higher LDH loadings[32] and could be due to a catalytic degradation effect that the LDH had on PP thus changing the thermal decomposition mechanism of PP.[31] Other possibilities for the decrease in thermal decomposition temperature of PP are the release of adsorbed water and the decomposition of the surfactant present in the LDH interlayer.[32] However, other work reported that the thermal stability of PP improves with LDH addition—the thermal degradation temperature increased by 70 °C compared to PP when Zi-Ti SDBS LDH was added to the matrix.[34] Due to increased char formation, high levels of residue were left behind at high temperatures for all the PP composite materials.[20,31–33] A similar decrease in thermal stability was observed in the thermal decomposition pathway of flame retardant (FR)/LDH/PLA composites, which could also be due to LDH/polymer interactions.[35] Further, the thermal degradation temperature of PNC was lower than pure PCL, possibly due to enhanced degradation caused by the OH groups present in the LDH structure or due to the earlier decomposition of LDH.[36] In consequence the thermal behavior of PNCs with LDH depend on the nature of the polymer, its general decomposition mechanism and the specific interaction with the LDH.

4.1.5 | Crystallization behavior

PCL is a biodegradable polymer that has a low melting point range, a low glass transition temperature, and poor mechanical properties, which limits its processability and widespread use. Commercial Mg-Al LDH was modified with stearic acid and SDBS and compounded with PCL.[36] The addition of both the modified LDHs did not impact the melting temperature of the PCL composites in a meaningful way. It did, however, change the crystallization of PCL. When stearate modified LDH was added to

PCL, the resultant composites had a slightly lower crystallization temperature. At a 3 wt% loading of SDBS modified LDH, the composite had a higher crystallization temperature than PCL. At higher loadings, a decrease in crystallization temperature was once again observed. Clearly, through the addition of LDH, one can modify the properties of the composite material when compared to the parent polymer.[36]

The measured crystallization and melting enthalpies of both SBDS and stearic acid modified Co-Al LDH/LDPE composites decreased with an increase in filler content, indicating reduction of LDPE chain mobility, which in turn hinders the formation of polymer crystal domains. This supports XRD findings that indicated good interaction between the LDH particles and matrix, leading to delamination/exfoliation.[26] The crystallization/melting behavior of composites prepared with Ni-Al LDH was not much different from pure LDPE, as determined with differential scanning calorimetry. When Co-Al LDH modified with stearate or palmitate was added to LDPE, a second, high temperature phase formed due to the effective interaction between polymeric chains and the LDH particles. This high temperature phase is attributed to the formation of polymer crystals domain induced by the LDH filler particles. The proportion of the regular phase of LDPE and the high temperature phase was independent of filler content.[26]

In addition to aiding the thermal stability of the polymer, the addition of Mg-Al BHPPA LDH to PP also influenced the crystallization behavior of PP. The exothermic peak temperature for pure PP occurs at 119 °C, while the exothermic peak temperatures of Mg-Al BHPPA LDH/MAH-g-PP/ PP composites increase to up to 130 °C.[22]

4.2 | Tailored composite properties through functionalization of LDHs

It is clear that the addition of LDH to a polymer will influence the material properties of the final composite. Not only can LDHs be used to influence processing and mechanical properties, but also to create multifunctional nanofillers. By careful design, LDHs can be functionalized and then added to polymer matrixes. This is often done by intercalating certain anions which can make an LDH act, for example, as an anti-oxidant or a FR in PNCs. LDHs can also be used to color a polymer matrix, like pink Co-Al LDH or green Ni-Al LDH,[26] or by intercalating a specific dye into the LDH.

4.2.1 | Improving flame retardancy

Many polymer applications, such as electronic cases and cables, have a high flammability risk due to the environment in which they are used as well as the inherent flammability of polymers in general. Even in applications were exposure to heat or flames are not that common, improvement of polymer flame retardancy is still important in order to protect against loss of property or life in the event of a fire. The use of a FR in a polymer composite as an additive is therefore important. Several types of FRs exist, including phosphorous or metal oxide containing compounds as well as halogenated FRs. However, halogenated FRs release toxic smoke when burned, metal hydroxides are required in large quantities to obtain satisfactory flame retardancy, and phosphorus-based FRs produce acidic substances after burning. LDHs are possible alternatives to these conventional FRs. LDHs decompose endothermically, releasing water vapor and forming a metal oxide residue. This means that LDHs can actively participate in flame inhibition during combustion by acting as an energy sink and can also provide a metal hydroxide type flame-retardant mechanism.

Some of the earlier work at the Leibniz-Institut für Polymerforschung PF used commercial Mg-Al LDH that was organo-modified with SBDS to improve the flammability of different polymers.[20,30–33] As already discussed, the addition of LDH changes the thermal decomposition behavior of the polymer matrix. This also affects the flammability of the PNC. During decomposition of PP/LDH composites, the release of adsorbed water and the catalyzed degradation/carbonation of PP, leading to char formation, reduced the initial flammability of the polymer.[32] Upon the ignition of PP, a char layer can slow down the heat release, protecting the underlying matrix from being consumed by the flame. In addition to slowing the heat transfer rate, the char layer can form a barrier that prevents the release of volatile gaseous decomposition products. Thus, the lower thermal stability is an advantage. Char formation was noticed in all LDH/polymer composites and increased with an increase in LDH loading.[20,31–33,37]

Several parameters related to the burning properties of a composite are determined using a cone calorimeter or a microscale combustion calorimeter. Heat release rate (HRR) controls how fast a fire could reach an uncontrollable stage. The addition of different organo-modified LDH to different polymers (PP, LDPE, PLA, and polyamide) reduced the peak heat release rate (pHRR) of the material, and also flattened the HRR curve.[20,21,30,31,33,35,37] The total heat released (THR) is related to how big a fire is and is often taken as the measure of the propensity to sustain a fire for long duration. Increasing the LDH concentration, whether it be Mg-Al SBDS or Co-Al SDBS or Zn-Al SDBS, reduced the THR of different composites.[20,21,30,31,33,35,37] The reduction in THR is likely due to the endothermic decomposition of LDH that acts as a heat sink and reduces the overall generated heat. The heat release capacity

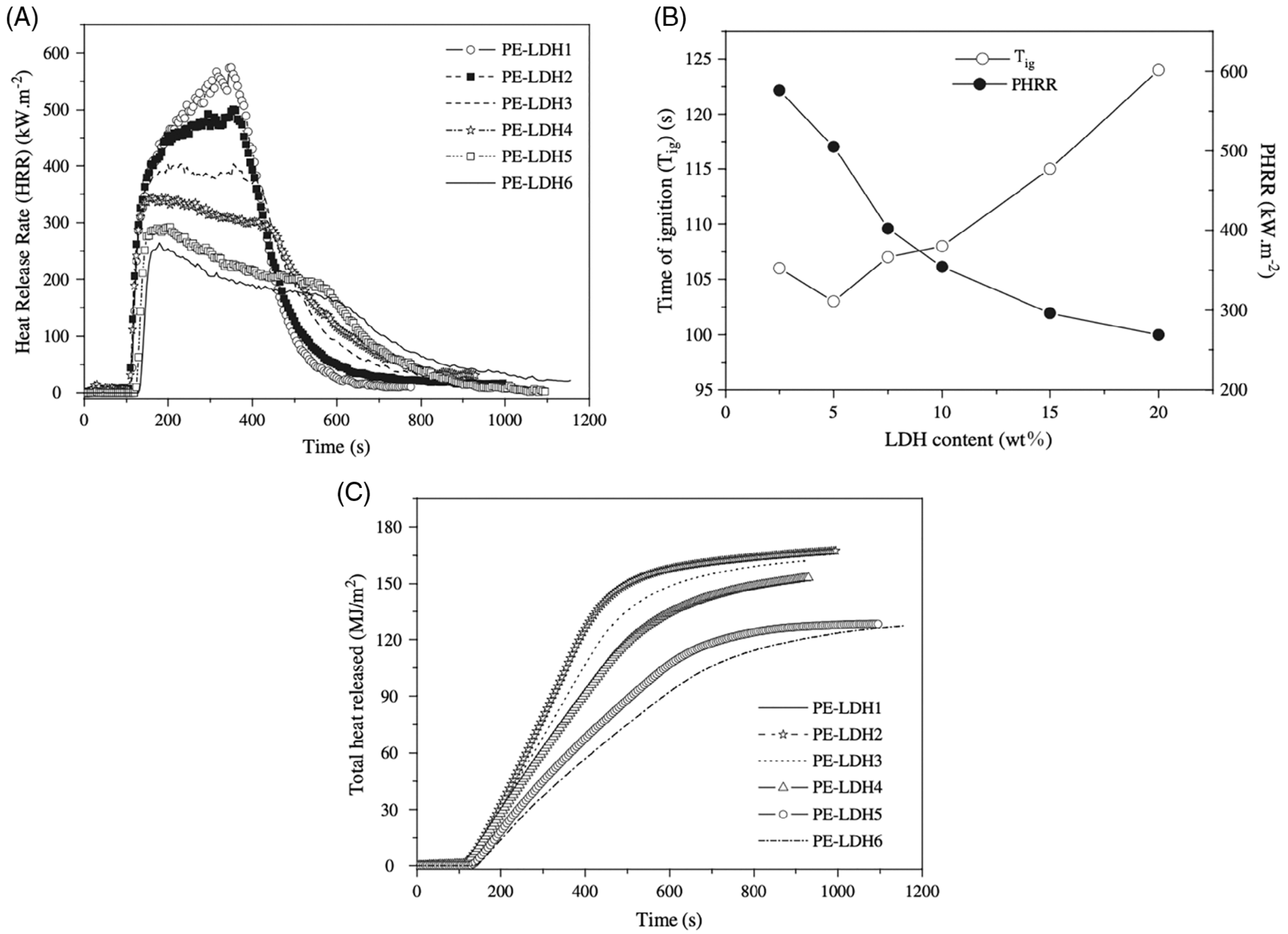

FIGURE 16 Cone-calorimeter investigation results showing (A) variation of heat release rate (HRR) with time, (B) variation of T_{ig} and peak heat release rate (pHRR) with layered double hydroxide (LDH) content and (C) total heat released (THR) with time in LDPE/LDH nanocomposites with increasing LDH concentrations (the sample was designated as PEXLDH, where X represents the weight percent of LDH). Reproduced with permission.[30] 2007, Elsevier.

(HRC) of polymer/LDH composites was also lower than that of the pure polymer[31,35,37] or, in the case of PLA and FR composites, lower than just the polymer and FR.[33] In LDPE composites the ignition time (T_{ig}), also increased with increasing LDH loading.[30] However, T_{ig} of PP composite materials was shorter than pure PP when Zn-based LDH structures were used.[20] This is consistent with the lower decomposition temperature of PP nanocomposites and the different degradation mechanisms of PP and PE. An example of the typical cone calorimeter results of LDH-based PNCs are shown in Figure 16.

The limiting oxygen index (LOI) is the percentage of oxygen required for self-sustained combustion of any material. When compared to pure LDPE, the LOI value of Mg-Al SDBS LDH/MAH-g-PE/LDPE composites was reduced when 2.43 and 4.72 wt% Mg-Al SDBS LDH was used. At higher LDH loadings, the LOI values increased with an increase in LDH concentration.[30] This is due to the difference in burn behavior of the test pieces at different LDH loadings. At low LDH concentrations, the thin layer of char is not an efficient barrier. Further, the viscosity of the molten polymer below the char is not sufficient to hold the char layer on the vertical test specimen. As a result, it flows down continuously and a fresh unburnt surface is exposed to flame causing continuous burning at a relatively lower oxygen concentration. At higher LDH loadings, the resultant char layer is thick enough to limit heat conduction through the char layer, meaning it acts as a physical barrier protecting the rest of the sample. At higher loadings more LDH can endothermically decompose, reducing the overall heat released by the flame. This makes the molten (not yet burning) polymer below the char more viscous. Therefore, it can support the char layer, preventing it from sliding down to expose unburnt material.[30] The Mg-Al SDBS LDH/LDPE nanocomposites did not pass any of the vertical UL94 specifications. However, the time at which dripping starts during the vertical UL94 test was significantly increased by the presence of LDH. The composites did pass the horizontal UL94 rating and showed a steady decrease in the rate of burning with increasing LDH loadings. Increasing the LDH loading even further results in an opposite effect. Due to the presence of a high amount of LDH the intercalated surfactant acted as a fuel due to its comparably low molecular weight. Overall, although Mg-Al SDBS LDH alone at these concentrations was not sufficient to obtain high LOI value or V0 rating in UL94 testing, the potential of its use as a FR was clear.

As toxic smoke is responsible for many deaths in accidental fires, the ability to suppress smoke production is another important function of FRs. Zinc-based compounds are effective at improving char formation and smoke suppression in burning polymers. Therefore binary Mg-Al LDH and ternary Mg-Zn-Al LDH was used in order to improve the fire resistance and smoke suppression of PP.[20] The LDHs were prepared with the one-step method and organo-modified with SDBS. In addition to the LDH, an intumescent flame retardant (IFR) was also added to the polymer composite. A synergistic char formation effect between the LDH and IFR was established. All the PP composites containing LDH showed lower total smoke production, likely by inhibiting the conversion of PP to volatile organics. The ternary Mg-Zn-Al LDH was more effective at smoke suppression and char formation than the binary Mg-Al LDH due to the introduction of zinc. In the UL-94 vertical burning test, PP composites except the 4 wt% binary Mg-Al LDH composite had high LOI values and could pass the V0 rating. The difference in binary and ternary LDH efficiency was due to the thermally stable and compact char layer which is formed by the Mg-Zn-Al LDH which effectively suppressed the spread of the flame and finally extinguished the fire. As expected, the addition of the FRs also affected the mechanical properties of the composites, lowering TS but increasing Youngs modulus. Overall, the composite prepared with 18 wt% IFR and 2 wt% ternary Mg-Zn-Al LDH had the most balanced mechanical properties, the best quantity and quality of char formation, and the best resistance to burning. The use of LDH together with a FR is not unique to this study. The addition of Mg-Al SDBS LDH or Zn-Al SDBS LDH together with a FR improves flame retardancy of PLA more than if the FR was used alone.[35] Organo-modified Zn-Al SDBS LDH was more efficient at improving flame retardancy of PLA.

Several common LDH modifiers are flammable surfactants, including SDBS. This could decrease the flame retardancy effect of the modified LDH in the final composite material. This is supported by a small increase in HRR in SBDS modified LDH/PP composites between 410 and 450 °C, which corresponds with the combustion of the intercalated SDBS anion.[31] Kang and coworkers[21] successfully prepared Mg-Al LDHs modified with acid yellow 36 (AY36) and acid red 88 (AR88) using the one-step method. The dye intercalated LDH was used to prepare polypropylene-grafted maleic anhydride (PP-g-MA)/LDH composites, which were compared with a composite prepared with a Mg-Al LDH containing interlayer $NO^{3-}$and SDBS. The addition of any of the LDHs improved the FR properties of the MAH-g-PP but AY36 and AR88 intercalated LDHs were the most effective. The decrease in the flammability is likely due to charring effects of sulfuric acid generated from the thermal decomposition of the sulfate dyes. Inorganic NO^{3-} intercalated LDH and SDBS intercalated LDH performed nearly identically, indicating that intercalated flammable surfactants might not be a big concern with regards to composite flammability as a whole.

Thermal decomposition behavior of PNCs can be compared to the activation energy of thermal decomposition as calculated by the Kissinger method. A clear increase in the activation energy with an increase in LDH content was observed.[31] This suggests that the organo-modified LDH makes the thermal decomposition of the composite more difficult.[31] Similarly, the Flynn–Wall–Ozawa and Friedman methods can describe the thermal degradation behavior of PNCs kinetically by relating the different thermal behaviors to the inherent active energies of the composites.[32] Both methods determined higher activation energies of the composite materials, that increase with an increase in LDH content, than that of pure PP. This could be an internal reason for improvement of the flame retardancy.[32]

4.2.2 | Increasing UV stability

Polymers are often used in environments where they are exposed to sunlight. This generally leads to photodegradation of the polymer, as sunlight causes the formation of free radicals in the polymer. Therefore, UV light protection of polymers is common and important. Different strategies are deployed, including using UV light absorbers, hydroxide decomposers, and radical scavengers. Various organic and inorganic commercial additives exist, although their use is not without problems. Organic UV stabilizers often leach out of polymer composites when used at high loadings, causing poor long-term efficiency and environmental damage. Common inorganic UV stabilizers, like titanium dioxide (TiO_2) and zinc oxide (ZnO), often make polymer composites opaque and can negatively affect the mechanical properties of the material. The use of LDH structures as UV stabilizers in polymer composites provides the opportunity to combine organic anions with inorganic cations in order to optimize their effectiveness.

For example, Mg-Al LDH modified with an azo dye 3-(4-anilinophenylazo) benzenesulfonic acid was used to stabilize PP.[38] LDH modification was confirmed with the typical analysis techniques. By intercalating the dye into the LDH structure, its thermal stability was increased. After compounding, the azo dye modified LDH/MAH-g-PP/PP composites showed good distribution of the LDH particles in the polymer matrix, although no intercalation of PP chains into LDH galleries, exfoliation of the LDH platelets or delamination of the metal hydroxide layers was observed on the XRD spectra. As the LDH could shield the dye during processing, the nanocomposite maintained the dye derived UV-absorption property. The intensity of UV absorption bands increased proportional to the dye intercalated LDH loading. When only the dye was added to PP, its UV-absorbing functionality deteriorated. The addition of inorganic LDH, dye modified LDH and dye by itself improved the TS and of the PP during aging. Further, dye modified LDH and azo dye alone improved PP durability. However, organo-modified azo dye intercalated LDH composites performed the best. As aging time increased, the bigger the difference in TS and the clearer it was that modified LDH provided the biggest reinforcing and stabilization effect. Overall, durability of PP was increased by more than four times by integrating dye modified LDH to polymer under accelerated weathering conditions.

LDHs with different TM combinations could also be used as UV stabilizers in PP.[34] Specifically, Zn-Ti, Zn-Sn, Zn-Ga, Zn-Cr, and Cd-Cr LDHs were studied.[34] UV–vis spectroscopy showed that the different LDHs had different UV–vis absorption behaviors. Zn-Ti LDH and Zn-Sn LDH both had a strong single UV–vis absorption peak in the UV–vis range of the spectra. In fact, Zn-Ti LDH exhibited similar UV absorption behavior to commercially used TiO_2 and ZnO. In order to improve the dispersion of the Zn-Ti LDH in the polymer matrix, the LDH was organo-modified with SDBS and LA by anion exchange. Both modifications were successful. After compounding the modified LDH with PP-grafted maleic anhydride, which was added to improve filler/matrix interaction, and PP the XRD spectra of the resultant composite suggested that there was intercalation of the PP into the LDHs. TEM images confirmed good dispersion of the organo-modified LDH particles in the PP matrix. Both the organo-modified Zi-Ti LDHs improved the UV stability of the polymer composites. The same effect was not seen with unmodified Zi-Ti LDH and Zn-Sn LDH. Zi-Ti SDBS LDH/PP composites absorbed the widest spectrum of UV light, as seen in Figure 17, and had the highest stabilization effect on PP against photo-oxidation.[34]

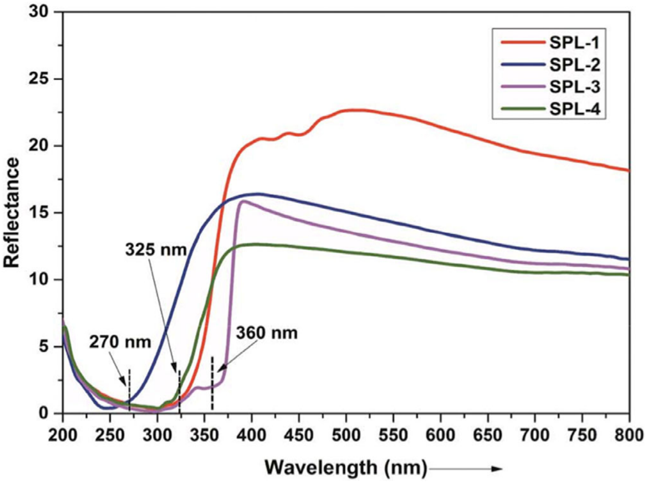

FIGURE 17 Ultraviolet–visible (UV–Vis) reflectance spectra of polypropylene/layered double hydroxide (PP/LDH) composites where 5 wt% Zn-Ti LDH (SPL-1), or Zn-Sn LDH (SPL-2) or, Zn-Ti SBDS LDH (SPL-3) or Zn-Ti LA LDH (SPL-4) was added to PP. Reproduced with permission.[34] 2018, RSC Publishing.

More recently, the use of layered hydroxide salts (LHSs) in polymer nanocomposites has been proposed. In LHSs, a fraction of the structural hydroxide groups in the layered brucite-like structure are substituted with oxo-anions or water molecules. LHSs have a typical plate-like morphology and present the general formula $(M^{x+}(OH)_{2-x}(A^{m-})_{x/m}{\cdot}nH_2O)$, where M^{x+} is a divalent metallic cation and A is an intercalated counterion with charge $m-$. As with LDHs, different anions can be intercalated, including complex organic molecules. *p*-aminobenzoate, which is derived from *p*-aminobenzoic acid (PABA), can be used to modify the UV absorption of the LHS. Gomez[39] prepared cobalt hydroxide nitrate (CoHN) and cobalt hydroxide *p*-aminobenzoate (CoHAB) to determine if these compounds can be effective at protecting polymers from UV degradation. CoHN was prepared with a modified urea hydrolysis method, and the CoHAB was obtained via anion exchange. Typical characterization techniques confirmed that the intercalation of the *p*-aminobenzoate anion in the cobalt hydrated salt was successful and that the modified LHS was plate-like. The thermal decomposition behavior of CoHAB was also different from CoHN, with an additional initial step where absorbed and intercalated water was released. Sodium *p*-aminobenzoate absorbs UV light in the range of 200–350 nm. In addition to broader UV light absorption, CoHN and CoHAB also absorbs visible light. The structure of CoHN was preserved after incorporation in the LDPE. With the addition of CoHAB into the polymer, the basal diffraction peaks were broadened, indicating that the material probably begins to undergo partial delamination. Electron microscopy showed that the LHS particles were distributed well in the LDPE matrix, with some agglomeration present. Void formation around the agglomerates suggests poor filler/matrix interaction. The addition of both CoHN and CoHAB to LDPE improved the UV absorption. The composites have maximum absorption peaks at 274 nm and, in the case of CoHAB, additional ones at 593 and 637 nm. Overall, the composites were effective at UV absorption between 250 and 400 nm. Following weathering for 300 h, the Fourier transform infrared (FTIR) spectra of pure LDPE and the composites were compared to determine if the increase in UV absorption combatted polymer degradation. The C═O:—CH band area ratio was used as a carbonyl index. The carbonyl band of the LDPE/CoHAB composite showed an increase in relation to pure LDPE after the same weathering conditions. The LDPE/CoHAB composite had the highest C═O:—CH ratio. Therefore, although CoHAB can absorb UV radiation, the weathering tests indicated that LDPE/CoHAB generates a higher concentration of carboxyl groups than the neat LDPE under the same weathering conditions. In contrast, the C═O:—CH ratio of the CoHN composite were 67% less than that of pure LDPE. This means that CoHN has a protective effect against polyethylene UV degradation.[39]

4.2.3 | LDH as an antioxidant

Polymers are susceptible to oxidative degradation during processing and long-term outdoor applications. Therefore, the stabilization of polymers via antioxidants is common. Unfortunately, antioxidants themselves often have low thermal stability, leading to oxidization during polymer processing at high temperatures. Another hindrance in their use is the fact that they can leach out from the polymers through migration, evaporation, and extraction. Incorporating such antioxidant molecules into LDH galleries offers a possible solution to these problems.

After the study on anti-oxidant modification of Mg-Al LDH discussed above,[15] its effectiveness in a polymer composite was tested.[22] Typical analysis suggested that the LDH particles were well dispersed, with polymer intercalation and partial exfoliation. The initial temperature of degradation of the composites prepared with Mg-Al BHPPA LDH was almost 23 °C higher than that of pure PP, and the decomposition temperature increased by 38 °C. Clearly the oxidative degradation of PP was delayed significantly because of the radical scavenging effect of the anti-oxidant intercalated LDH. The anti-oxidant activity of the composite materials was studied by UV–vis spectroscopy after reaction with DPPH radicals. The FTIR spectra of the composites showed the same photoproducts as pure PP. Therefore, the mechanism of oxidation of the polymer is not modified by the presence of the clay. The presence of the antioxidant has a significant effect on the induction time, delaying the onset of oxidative degradation by about 10 h when the anti-oxidant alone was added to PP. However, when the anti-oxidant was intercalated into the LDH, this induction time was increased by 22 h compared to pure PP. Clearly the longevity and activity of the BHPPA anti-oxidant increased after intercalation in the Mg-Al LDH. It is worth noting that unmodified LDH reduced the induction period dramatically.[22]

4.2.4 | Novel applications of LDH-based polymer nanocomposites

In addition to aiding or replacing additives found commonly in polymer processing, LDHs can also be used to impart more novel properties to composite materials. This concept of using multifunctional nanofillers is gaining popularity, leading to the design of new nanofillers for advanced applications. In the case of LDHs, the inorganic part can improve the mechanical, gas barrier, and thermal properties of a composite, while the organic anion can have functional groups capable of providing new properties.

4.2.5 | Conductive composite materials

Kutlu and coworkers[40] successfully prepared polyaniline (PANI) modified LDH as an additive to MAH-g-PE to improve its conductivity and flame retardancy. Such a polymer composite would be well suited for the electrical cable industry by being FR and able to eliminate the buildup of electrostatic charge on the outer surface of the cable. In order to increase the basal spacing of the Mg-Al LDH as well as its polymer matrix compatibility, the Mg-Al LDH was modified with SDBS via reconstruction. The solubility and conductivity of PANI synthesized by different methods and with varied doping agents were investigated. Acetic acid protonation (PANI/AA) gives the highest conductivity, followed by dodecylbenzenesulfonic acid protonation (PANI/DBSA) while hydrochloric acid protonation (PANI/HCl) had the lowest conductivity. As conductive polyaniline shows poor organosolubility, hindering LDH intercalation or adsorption, the emeraldine bases were used to modify the LDH. To repair the lost conductivity, camphorsulfonic acid (CSA) was used as redoping agent. CSA had good compatibility with the organo-modified LDH, leading to a good recovery of conductivity after converting emeraldine bases to their salt form. In fact, the conductivity of the PANI/DBSA modified LDH increased to 265 μS cm^{-1} (compared to 79 μS cm^{-1} of the original PANI/DBSA). PANI/DBSA modified LDH showed much higher conductivity than the initially doped PANI/AA and the PANI/AA and PANI/HCl modified LDH. The good organosoluble characteristic of the de-doped PANI/DBSA emeraldine base provided a successful embedment of PANI chains through the LDH layers. The MAH-g-PE/ PANI/DBSA modified LDH composite had a conductivity of 1.1 μS cm^{-1} which, although lower than of the modified LDH and PANI/DBSA, is still within the required range of 0.01 and 10 μS cm^{-1} to be classified as an electrostatic dischargeable material. XRD, TEM and rheology suggest a good distribution of the LDH in the matrix, with exfoliation of some of the platelets. However, agglomerates of LDH particles were also observed, and no continuous phase of PANI was found. Therefore, the derived conductivity of composites originated from nanodispersed PANI modified anionic clays.

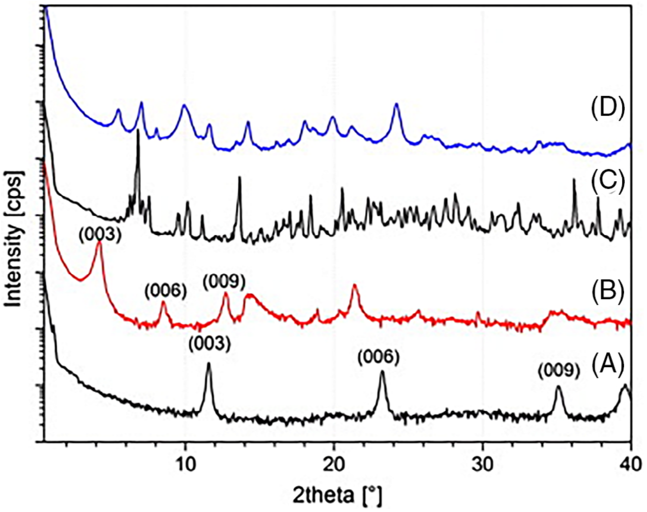

FIGURE 18 X-ray diffractograms of (A) pristine layered double hydroxide (LDH), (B) camphorsulfonic acid (CSA) modified LDH, (C) sodium salt of ciprofloxacin, (D) ciprofloxacin modified LDH. Reproduced with permission.[41] 2104, Elsevier.

4.2.6 | Bio-medical applications

The development of materials with anti-microbial properties is important for new solutions to limit the spread of bacteria and consequently lower the risk for diseases, especially in the current state of increased antibiotic resistant bacteria. To this end, Mg-Al LDH organically modified with CSA and ciprofloxacin was prepared via ion exchange.[41] Typical characterization techniques, including XRD analysis, shown in Figure 18, confirmed the successful intercalation of CSA into the Mg-Al LDH interlayer galleries. However, the modification of LDH with ciprofloxacin was not as successful. In fact, unmodified Mg-Al LDH and ciprofloxacin were found to coexist with some modified LDH. The reason for that difference in behavior might be found in the functional groups of CSA, which has a sulfonic acid group, and ciprofloxacin, which has a carboxylic acid group. The intercalation of CSA into LDH improved its thermal decomposition resistance significantly. This LDH shielding was necessary for the subsequent processing of CSA modified LDH composites. The modified LDH was then used to prepare anti-microbial HDPE fibers. The fibers were produced in a multi-step process: first MAH-g-PE and an LDH were mixed, next the masterbatch was diluted in HDPE, using a compounder, and then the nanocomposite was melt-spun using a piston-type spinning device.

The manufacturing technique of fiber spinning LDH/polymer nanocomposites that was previously developed was scaled-up.[42,43] Carboxylic acid salt modified LDHs were melt-mixed with HDPE, at concentrations of up to 3 wt%, and MAH-g-PE compatibilizer before being melt-spun. The mechanical properties of melt-spun fibers were influenced by several different parameters like processing parameters, filling degree, and/or collateral factors such as photodecomposition and storage time. Tetradecanoic acid modified LDH at 1 wt% filler loading was found to give the most notable results.

The CSA and ciprofloxacin LDH/MAH-g-PE/HDPE composites did not exhibit typical rheological behavior. Addition of the filler led to a small increase in viscosity, but no notable shear thinning effect was observed in the low frequency zone. This is likely due to limited filler–filler and filler–matrix interactions at the low loadings used in this work (1.34 wt% CSA—and 0.95 wt % ciprofloxacin modified LDH), taking into account a typical concentration of the antibiotics in an active formulation. The modified LDHs were predominantly distributed throughout the matrix as small aggregates. These agglomerates were smaller than 100 nm so the composites were suitable for melt-spinning. Overall, Mg-Al CSA LDH was better distributed with partial intercalation and exfoliation of the particles. The fibers were tested against seven different Gram-negative bacteria and Gram-positive bacteria. Fibers containing CSA modified LDH showed antimicrobial activity against Gram-positive bacteria, while ciprofloxacin containing fibers were effective against both Gram-positive and Gram-negative bacteria. Examples of the spun fibers' effect on different bacteria can be seen in Figure 19. Elucidation tests showed a remarkably low leaching rate for CSA/LDH nanocomposites, whereas

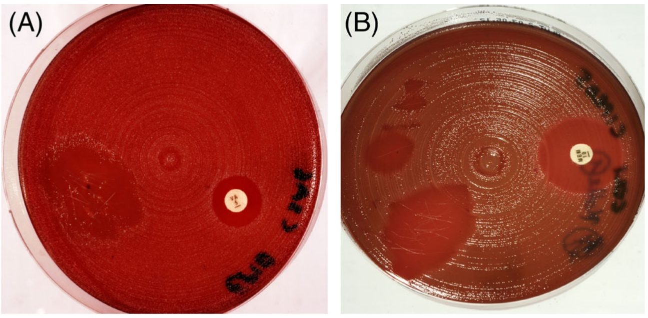

FIGURE 19 The bacterial growth of (A) *Staphylococcus epidermidis* against 1365 mg L^{-1} camphorsulfonic acid (CSA) integrated layered double hydroxide/polyethylene (LDH/PE) and (B) *Escherichia coli* against 1365 mg L^{-1} ciprofloxacin integrated LDH/PE. Reproduced with permission.[41] 2014, Elsevier.

ciprofloxacin/LDH nanocomposites showed bisection after 70 h in ethanol. These results stimulate further research about the mechanism of inhibition in the case of LDH-CSA nanocomposites.

4.2.7 | Multiwalled carbon nanotubes decorated with LDHs

Carbon nanotubes (CNTs) are popular one-dimensional (1D) nanofillers for polymers due to their high strength, stiffness and large aspect ratio. CNTs are also effective at enhancing the crystallization rate of semi-crystalline polymers and as FRs in polymers. However, the dispersion of CNTs within the polymer matrix is challenging, especially at higher loadings. Surface modification or noncovalent wrapping methods are effective for the homogeneous dispersion of these fillers in polymers. One possible solution to this problem is to combine CNTs with LDHs to form three-dimensional (3D) hybrid nanomaterials with enhanced filler properties as well as increased ease of dispersion.[44] Therefore, hierarchically organized CNT-LDH hybrids were prepared by mixing negatively charged functionalized CNTs with exfoliated and fragmented positively charged Co-Zn-Al LDH using an ultrasonic-assisted layer-by-layer assembly process.[44] These CNT-LDH hybrid fillers were then used to prepare isotactic polypropylene (iPP) nanocomposites via a solution blending method. FTIR and TEM analysis confirmed that the delaminated and fragmented LDH particles are decorated on the surface of the CNTs. WAXS spectra and TEM images of the nanocomposites suggested that the CNT-LDH hybrid particles were well distributed in the matrix. The addition of CNT-LDH hybrids to iPP improved the thermal stability and flame retardancy of iPP significantly, even at only 2 wt% loading as shown in Figure 20. Decomposition temperatures increased, residual char increased, HRR values decreased by 59% and the LOI increased to 23% for these nanocomposites. Further, a synergetic effect between CNTs and LDH was found that surpasses individual nanofillers as effective FRs due to the formation of a jammed network in the polymer matrix and effective char formation that restricts the transport of volatile compounds during the burning of the polymer.

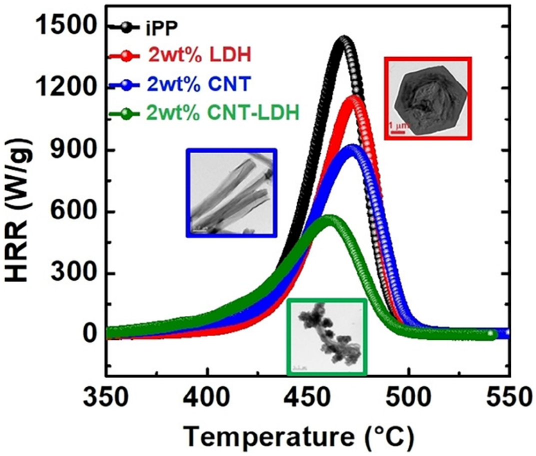

FIGURE 20 Heat release rate (HRR) curves of isotactic polypropylene (iPP) and iPP composites with layered double hydroxide (LDH), carbon nanotube (CNTs), and functionalized LDH-CNT showing the increase in fire resistance of iPP, as well as transmission electron microscopy (TEM) images of Co-Zn-Al LDH (red), functionalized CNTs (blue), and CNT-LDH hybrids(green). Reproduced with permission.[44] 2022, John Wiley and Sons.

5 | LDHs IN RUBBER COMPOSITES

Elastomers are polymers that can undergo chemical reactions to form chemical bonds between the polymer chains when heated. This forms a flexible polymer network with high mobility that can undergo large elastic deformations without breaking.[45] LDHs have been used as reinforcing fillers and functional additives in thermoplastics as discussed above for several years due to the ease of synthesis and ease of customization of LDH. More recently, LDH has gained interest as a reinforcing and functional filler in various elastomers. Several studies have been done to investigate how LDH can affect the crosslinking process, mechanical properties and other properties such as fire retardancy of various elastomers.

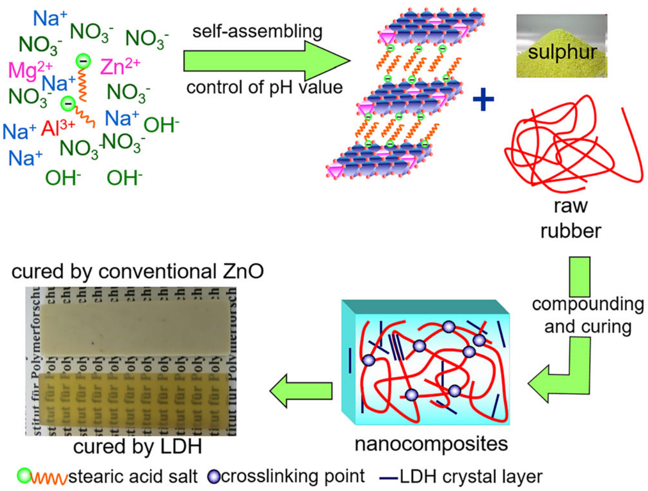

FIGURE 21 Schematic presentation for the preparation procedure of layered double hydroxide (LDH) (LDH-St) and rubber/LDH-St composites. Reproduced with permission.[47] 2011, RSC Publishing.

Stearic acid and ZnO are two components of the sulfur vulcanization system. In recent years there has been some concern over the negative effect that ZnO can have on aquatic life.[46] Because of this, an effort has been made to reduce the amount of ZnO used in rubber. A Mg-Zn-Al LDH modified with stearic acid could serve as a replacement for ZnO and stearic acid in the crosslinking system in nitrile butadiene rubber (NBR), solution styrene butadiene rubber (SSBR), chloroprene rubber (CR), natural rubber (NR), and carboxylated butadiene rubber (XNBR), with only a tenth of the Zn usually provided by ZnO being required for crosslinking.[47] The stearate modification compatibilized the LDH and elastomer matrix, allowing partial exfoliation and polymer chain intercalation to take place. The LDH cure was more efficient than the standard cure. The partial exfoliation of the LDH platelets increased the surface area of the LDH. This increased the amount of Zn available to participate in the crosslinking reactions and thus increased the crosslinking efficiency. In comparison, the Zn ions in ZnO are mostly in the bulk crystal and can therefore not participate in the reactions. Because of this, a lower concentration of Zn is required for crosslinking than when ZnO is used. Interestingly, the composites containing LDH were also transparent, as shown in Figure 21. The TS of the composite cured with LDH was comparable to the standard cure but had a lower elongation at break (EB). The reduction in EB is most likely due to the increased crosslink density of the LDH cured composite. The LDH layers also act as a barrier to oxygen, slowing oxidative cleavage and causing the mechanical properties to be retained better than the standard cure.

Wang[48] prepared a flame-retardant maleic anhydride grafted ethylene propylene diene monomer (EPDM) composite using Mg-Al LDH that was organically modified with SDBS, and an IFR consisting of pentaerythritol, ammonium polyphosphate and methyl cyanocacetate. The LDH was shown to be synergistic with the FR, significantly decreasing the HRR, reducing mass loss and resulting in low fire growth rate, as shown in Figure 22. This synergistic effect was seen even at low concentrations of LDH. It was proposed that the flame-retardant mechanism was due to the formation of char, shown in in Figure 23, caused by the decomposition of the LDH. The char layer could provide a barrier to heat transfer and volatiles.

Zn-Al LDH coated in stearic acid can be used as an alternative to ZnO in SSBR.[49] It was found that even at very high LDH loadings, the mechanical properties of the SSBR were improved, as the TS, EB and modulus all increased with increasing LDH content up to 80 phr LDH. Even at 100 phr, the LDH was uniformly dispersed, but polymer chain intercalation into the LDH did not take place and there was no exfoliation of the LDH platelets. Interestingly, a thermotropic effect was observed in some of the composites. As the temperature of the composites was increased, they became more opaque, and when cooled the composites became transparent again. At low LDH concentrations, there was no thermotropic effect, but as the LDH content was increased the thermotropic effect increased up to 60 phr LDH, where it reached a plateau. This novel thermotropic material be used as a potential smart material, as the thermotropic effect is achieved without sacrificing mechanical properties of the SSBR, for example, as a protective layer for temperature sensitive solar cells.

The use of LDH containing Zn was investigated further. Stearate modified Zn-Al LDH was added to NBR in the place of ZnO in both a sulfur cure and a peroxide cure.[50] As noted previously, the sulfur cure using LDH was still efficient when compared to a conventional cure system containing ZnO despite having a lower concentration of Zn ions. In the peroxide cure, the optimum cure time and the curing reactions were not affected by the addition of LDH, but the TS and modulus of the peroxide cured composites were increased when LDH was added, while EB was reduced. This shows Zn-Al LDH can be added to peroxide cured NBR without negatively impacting the cure system. Similarly to the previous results, the composites containing LDH retained their properties better than the samples cured using the standard cure systems.

In XNBR composites containing Zn-Al LDH, the unmodified LDH acted as a reinforcing filler and as an efficient alternative to ZnO in the curing system.[51] The LDH was well-dispersed in the XNBR matrix,

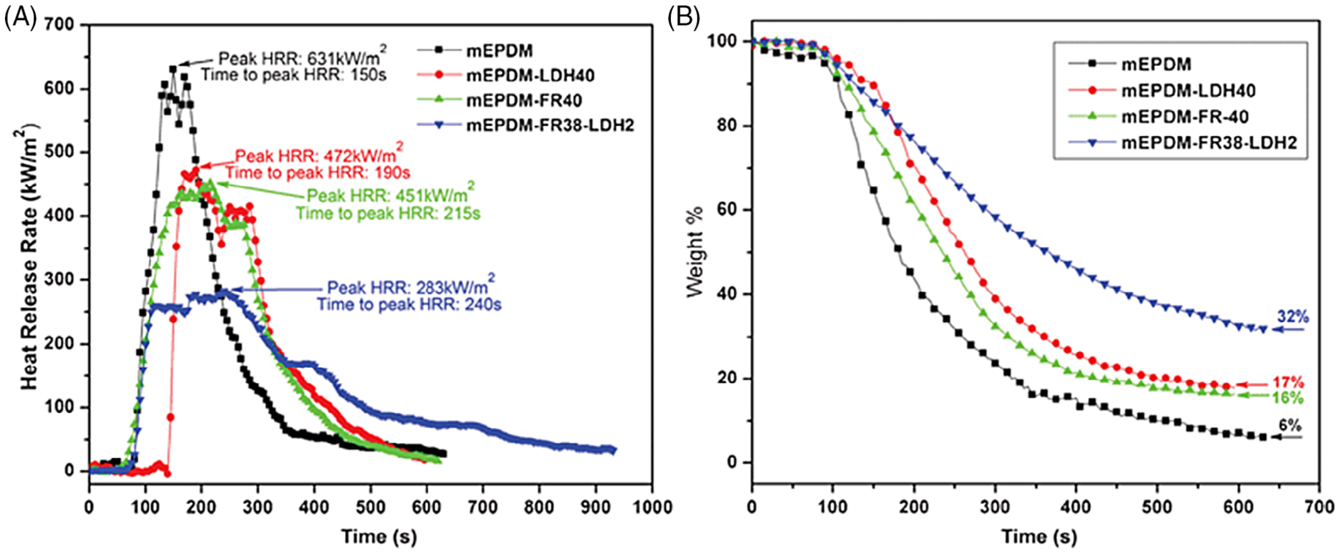

FIGURE 22 (A) Heat release rate (HRR) and (B) mass loss of EPDM samples from cone calorimeter test. Reproduced with permission.[48] 2012, RSC Publishing.

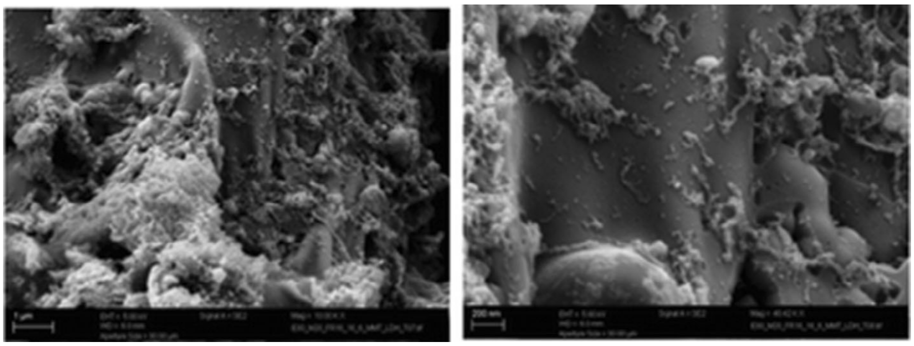

FIGURE 23 Scanning electron microscope (SEM) for the residue of the fire retarded EPDM/layered double hydroxide (LDH) nanocomposite after combustion. Reproduced with permission.[48] 2012, RSC Publishing.

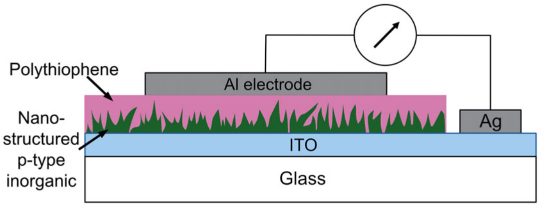

FIGURE 24 Schematic of a bulk heterojunction hybrid solar cell with $Co_5(OH)_8(NO_3)_2{\cdot}2H_2O$ incorporated as the active p-type material. Reproduced with permission.[57] 2009, Elsevier.

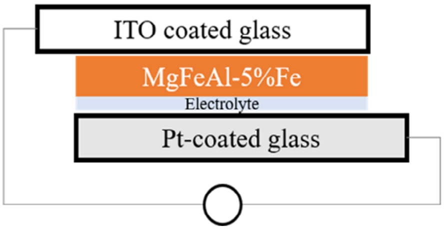

FIGURE 25 Schematic of layered double hydroxide (LDH) based solar cell. Reproduced with permission.[58] 2020, MDPI.

even at 100 phr LDH, although there was no exfoliation or intercalation. There was no filler network, which is uncommon at high filler concentrations. The LDH was chemically coupled to the XNBR and this, combined with the good dispersion of the LDH, resulted in good mechanical properties. The flame retardance of the composites was also investigated and it was found that the addition of LDH significantly reduced the PHRR and flattened the HRR curve. The total heat released was reduced by the LDH. The LDH undergoes endothermic decomposition, which acts as a heat sink and therefore reduces the total heat released during combustion and the LDH also forms a thermally insulating char layer. LDH therefore acts as a FR in XNBR.

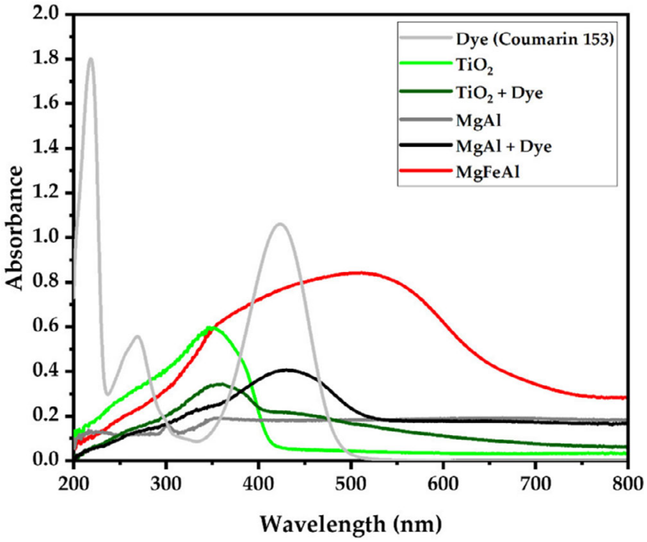

FIGURE 26 Ultraviolet–visible (UV–Vis) absorption spectra of dye, TiO_2, TiO_2 + dye, Mg-Al layered double hydroxide (LDH), Mg-Al LDH + dye, and Mg-Fe-Al LDH. Reproduced with permission.[58] 2020, MDPI.

6 | OTHER LDH COMPOSITE MATERIALS

Apart from polymer composites, LDH has also been used in other composite materials. A focus of the institute is the use of such composites in energy applications like solar cells and pseudocapacitors.

6.1 | Solar cells

The use of solar cells able to produce electricity from sunlight is a popular and sustainable alternative to fossil fuels. Several solar cell designs exist, including silicon solar cells and dye-sensitized solar cells (DSSC). These types of solar cells are not without problems, including cost, and in the case of DSSC, long-term stability of the dyes used, as well as the evaporation of solvents from and leakage of the electrolyte. Different strategies have been investigated to mitigate or eliminate these complications. Some include LDHs, like the use of LDHs as alternative wide bandgap semiconductors or in quasi-solid-state electrolytes.[52–56] A very simple approach to prepare solar cells was reported by Schwenzer,[57] shown in Figure 24. The design concept of such a photovoltaic device is good

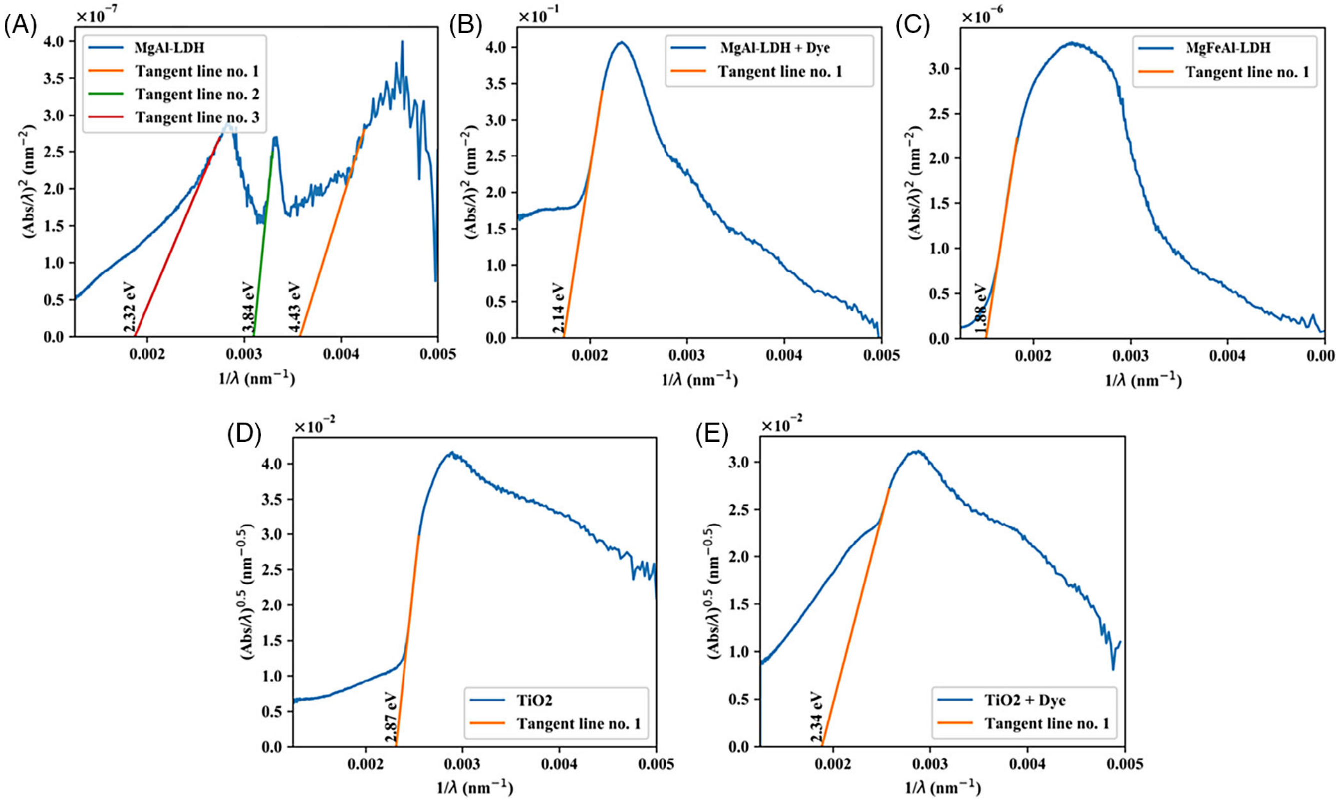

FIGURE 27 Bandgap determination of (A) Mg-Al layered double hydroxide (LDH) (2.32, 3.84, and 4.43 eV); (B) Mg-Al LDH + dye (2.14 eV); (C) Mg-Fe-Al LDH (1.88 eV); (D) TiO_2 (2.87 eV); and (E) TiO_2 + dye (2.34 eV) using the ASF method Reproduced with permission.[58] 2020, MDPI.

but with no practical value as the efficiency is very low (3.2×10^{-3}%) and preparation also involves difficult steps. Two solar cells consisting only of an LDH, either Mg-Al or Mg-Fe-Al, were compared with traditional DSSC made of Coumarin 153 dye and TiO_2 as well as a cell prepared with a combination of Coumarin 153 dye and Mg-Al LDH.[58] This was done to investigate if a photoactive LDH could act as a photo absorber. The LDH or TiO_2 was simply applied to an ITO coated glass as a paste and allowed to dry, before combining it with a Pt-coated glass counter electrode. Lastly, a high-performance electrolyte was injected between the two electrodes to complete the cell. A schematic picture is shown below in Figure 25 for this type of solar cell design based on LDHs.

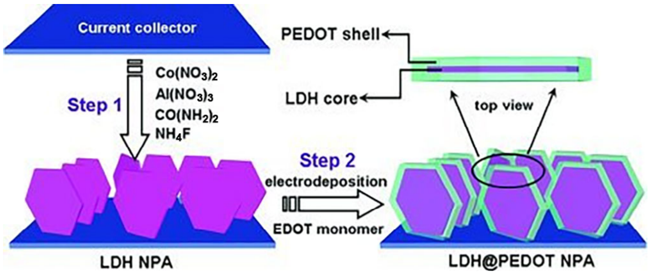

FIGURE 28 Schematic illustration for the fabrication of layered double hydroxide (LDH)@poly (3,4-ethylenedioxythiophene) (PEDOT) core/shell nanoplatelet array electrode taken from. Reproduced with permission[59] 2012, John Wiley and Sons.

The UV–vis absorbance of LDH was enhanced considerably with Fe substitution, as is clear from Figure 26. Compared to both dye photosensitized and plain LDH or TiO_2, Mg-Fe-Al LDH absorbed significantly more visible light and had similar UV absorption compared to plain TiO_2. Using the absorption spectrum fitting (ASF) method in Figure 27, the band gap of the Mg-Fe-Al was

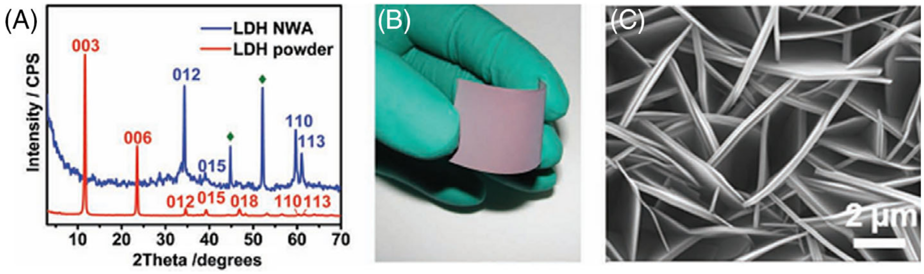

FIGURE 29 (A) X-ray diffraction (XRD) patterns, as well as the (B) optical and (C) top view scanning electron microscope (SEM) images of large-scale Co-Al layered double hydroxide (LDH) nanoplatelet array (NPA) on Ni film substrate. Reproduced with permission[59] 2012, John Wiley and Sons.

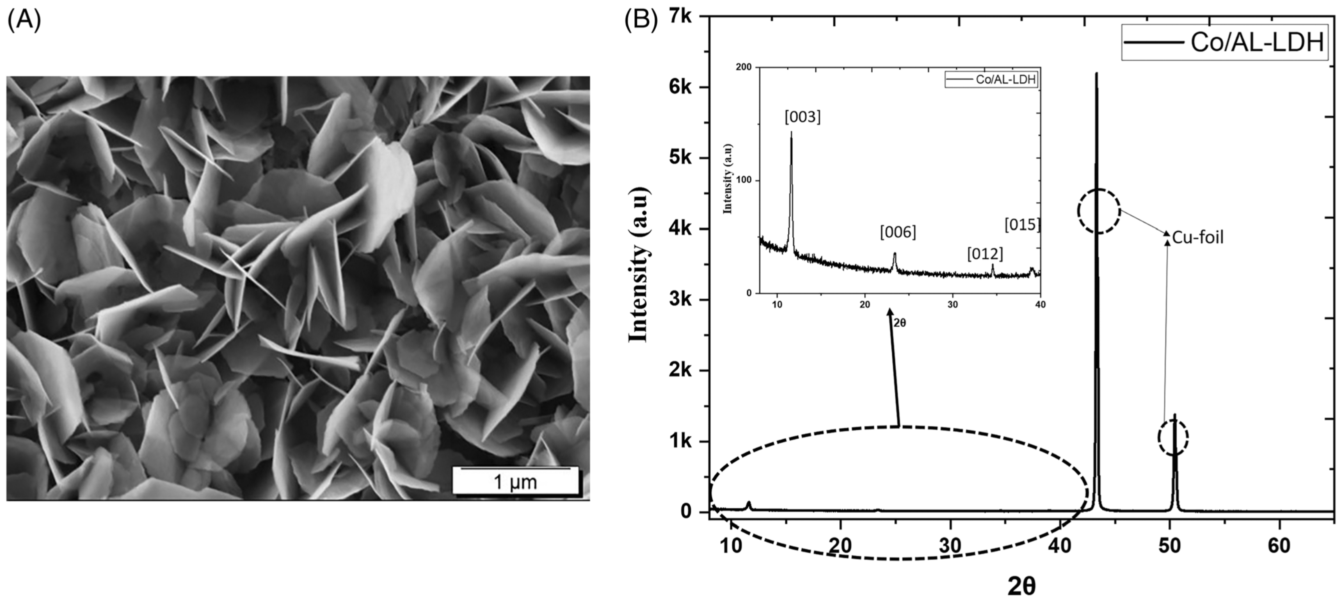

FIGURE 30 (A) Scanning electron microscope (SEM) image and (B) grazing incidence–small-angle X-ray scattering (GI-SAXS) reflections of Co-Al layered double hydroxide (LDH) on a copper film.

determined as 1.88 eV,[58] which was the lowest of all the materials and closest to the ideal band gap of 1.4 eV. The photovoltaic potential of the solar cells was determined using a multimeter and a solar simulator. Under the simulated AM 1.5 illumination, the solar cell prepared with Mg-Fe-Al LDH had an open circuit voltage (V_{OC}) of 726 mV. In comparison, the dye assisted Mg-Al LDH and TiO_2 solar cells had V_{OC}s of only 69 and 81 mV respectively. The plain Mg-Al LDH solar cell was totally non-functional. The Mg-Fe-Al LDH based solar cell outperformed all the other configurations with an energy conversion efficiency of 1.56%. This work clearly showed that it is possible to replace the dye and semiconductor complex used in dye assisted solar cells with a UV–Vis photo absorbing LDH.

6.2 | Pseudocapacitors

Another example of the use of LDHs in the energy sector is in a high performance flexible pseudocapacitor.[59] Electrochemical capacitors, or supercapacitors or ultracapacitors, are popular energy storage devices with high power density, long cycle life, short charging time and good safety record. Pseudocapacitors, also known as redox capacitors, are one type of supercapacitor that can achieve high specific energy due to fast and reversible redox reactions of the active material. LDHs have a high redox activity, which makes them possible pseudocapacitive materials. Han[59] prepared a Co-Al LDH@poly(3,4-ethylenedioxythiophene) (PEDOT) core/shell nanoplatelet array (NPA) on a flexible Ni foil. The preparation of the hybrid LDH@PEDOT core/shell NPA as a pseudocapacitive electrode involved two steps, as illustrated in Figure 28.

The XRD spectra in Figure 29A together with the top view SEM of the LDH on the Ni film in Figure 29C indicated a preferential orientation of LDH particles perpendicular to the film substrate. The good flexibility and robustness of the LDH NPA is shown on repeat bending in Figure 29B. Overall, the resultant LDH@PEDOT core/shell NPA had excellent electrochemical behavior, including a high specific capacitance 649 F g^{-1} based on the total mass by cyclic voltammetry (scan rate: 2 mV s^{-1}) and 672 F g^{-1} by galvanostatic discharge (current density: 1 A g^{-1}). Further, the flexible pseudocapacitor had a good rate capability with a specific energy of 39.4 Wh kg^{-1} at a current density of 40 A g^{-1}, as well as good long-term cycling stability. 92.5% of its original capacitance was retained after 5000 cycles. This is better than conventional supercapacitors and LDH NPA without the PEDOT coating. The enhanced pseudocapacitance of the LDH@PEDOT core/shell NPA was likely caused by synergy of the individual components. The LDH nanoplate core had a large energy storage capacity, while the PEDOT shell could provide electron transport during the charge–discharge process.

Neff and Leuteritz[60] developed CoAl-LDH structures on copper films by an adapted urea method with an area as large as 15 cm by 25 cm for such an application. SEM images and XRD with grazing incidence-small-angle X-ray scattering proved the development of LDH on the film. Nevertheless, obviously due to slight deviations in reaction temperature of less than ~1 °C completely different structures were found to develop as is shown in Figure 30.

7 | CONCLUSIONS

As inorganic LDHs are not compatible with organic polymers, the LDHs can be modified by exchanging the inorganic interlayer anions with organic anions. Several organo-modification methods exist. Reconstruction relies on the memory effect of LDH and is well suited to intercalating longer/bigger organic molecules. For efficient modification of LDH prepared by urea hydrolysis with smaller or bulky anions, a one-pot modification method that first replaces CO_3^{2-} by NO_3^{-}, before a surfactant/NO_3^{-} exchange takes place can be used. A simple one-step method, based on co-precipitation, was also developed and was extremely successful at LDH modification. Accurate pH control is required to prevent CO_3^{2-} contamination in the interlayer. In addition to enhancing polymer/LDH compatibility, exchanging the interlayer anion with larger organic anions also increases the interlayer distance in the LDH structure. This aids intercalation and exfoliation of LDH platelets during processing.

Once modified, LDHs can be incorporated into different polymer composites more easily. LDH nanocomposites show shear thinning behavior at low frequencies due to the presence of several domains of particle networks that exit in the matrix. The addition of LDH to polymers increases the stiffness of the polymer. Often, LDH also improves the thermal stability of the composites, but not in all polymers. In PP, LDH lowers the thermal stability of the polymer by catalytic degradation. LDHs are effective at reducing polymer flammability, suppressing smoke formation, increasing UV stability, and stabilizing polymer during processing. In order to prepare nanocomposites with special properties, LDHs intercalated with organic molecules with specific characteristics can be used. The hydroxide layers of the LDH act as a shield for the organic anions during processing, enhancing their stability. In addition to imparting a desired property, like anti-microbial activity, the organic molecule also aids with LDH dispersion and distribution. LDHs can also act as functional fillers in rubber to improve flame retardancy and as an alternative to ZnO during curing.

In all cases the complete production chain starting with the selection of ions for synthesis, the method of

LDH preparation, its modification with an eventually functional anion as well as the processing into a nanocomposite with an adequate polymer matrix has to be considered for an application. In that respect, LDHs offer a unique possibility to tailor polymeric materials to their specific use. Even after many years of research a plethora of ideas is still open to discover, where this review can give only a glimpse into possibilities, spanning from simple adsorption chemistry to sophisticated energy transport, conversion and storage.

ACKNOWLEDGMENT

Open Access funding enabled and organized by Projekt DEAL.

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How to cite this article: H. Oosthuizen, L. Jones, S. Naseem, F. J. W. J. Labuschagne, A. Leuteritz, *J. Polym. Sci.* **2023**, *61*(16), 1749. https://doi.org/10.1002/pol.20230025