Recent progress in polymer/layered double hydroxide nanocomposites*

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Abstract   New developments in the studies of nanocomposites based on polymer matrixes and layered double hydroxides (LDHs) in recent years are reviewed combining our relative research work, among which the synthesis techniques, the physicochemical characterizations, and the improved material properties are especially discussed. The possible application of polymer/LDH nanocomposites is also proposed.

Keywords: nanocomposite, layered double hydroxide, synthesis, characterization, structure, property.

Since the Toyota research group firstly reported the application of Nylon-6/montmorillonite (MMT) nanocomposites for automotive industry in 1993[1], polymer/layered silicate nanocomposites have attracted great interest, because these nanocomposites often exhibit dramatically enhanced mechanical performance, thermal stability, flame retardance, and gas barrier properties even with small loadings of layered silicate compounds compared with the conventional or micro-scale polymer/inorganic composites[2,3].

Polymer/layered double hydroxide (LDH) nanocomposites are rarely reported in recent literature. However, because of their highly tunable properties and unique anion exchange properties, LDHs are considered to be a new emerging class of the most favorable layered crystals for the preparation of multifunctional polymer/layered inorganic nanocomposites.[4]

In the present paper, recent progress in the studies of polymer/LDH nanocomposites is reviewed based on our relative research work[5—15], such as the synthesis techniques, the physicochemical characterizations, and the improved material properties. Moreover, the possible application of polymer/LDH nanocomposites is also discussed.

1   Layered double hydroxides

The LDHs belong to the anionic clay, whose structures can be described by the ideal formula,

$[M_x^{2+} M^{3+} (OH)_{2x+2}]^+ A_{1/m}^{m-} \cdot nH_2O$ ($M^{2+} M^{3+}$-A for short), where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively; A^{m-} is the interlayer anion, and x is the mole ratio of M^{2+} and M^{3+} (generally, in the range of 2—4). The typical structure of LDH material is presented in Fig. 1. It can be seen that the structure of LDH consists of brucite-like layers constituted of edge-sharing $M(OH)_6$ octahedra, in which the substitution of partial M^{2+} by M^{3+} induces positive charges in the LDH layers. The electrical neutrality is maintained by the anions located in the interlayer domains containing water molecules, wherein these water molecules are connected to both the metal hydroxide layers and the interlayer anions through extensive hydrogen bondings and can be removed without destroying the layered structures of LDH. [16]

LDHs have highly tunable properties. For example, the basic property of LDHs is the basicity, wherein the OH^- groups in the layers can react with other composites to introduce new properties into LDHs; LDHs also have partial acidity, which are influenced by acidity of the M^{3+} and M^{2+} hydroxides and the types of the interlayer anions; the versatile interlayer composition can be obtained by accommodating many different cations in the LDH layers; the interlayer anions can be exchanged by various anions using different methods; the anionic exchange capacity (AEC) of LDHs may be adjusted in a wide range
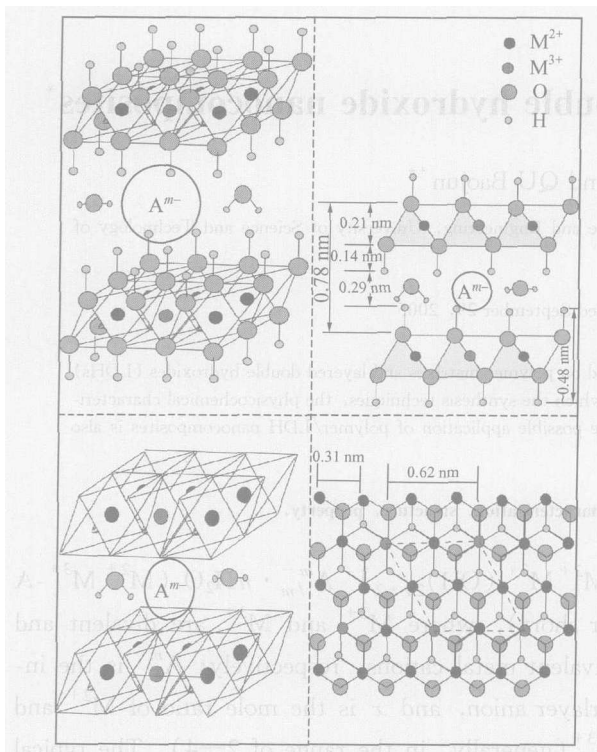
Fig. 1. Illustration of LDH's structure (hydrotacite as an example).

by changing the ratios of M^{3+} and M^{2+} [16—20]. These properties make LDHs become important layered crystals used as catalysts, catalyst support, flame retardants, stabilizers, medical materials, adsorbent, etc.

LDHs can be synthesized by various techniques, such as coprecipiation[21,22], structure reconstruction[23,24], sol-gel[25], hydrothermal synthesis[26], anion exchange method[27], and so on[28,29]. However, this does not mean that it is easy to prepare pure LDHs, but means that different techniques may be adopted to obtain the desired LDH compositions. Considering the different preparation methods, the coprecipiation is the most common and useful method to prepare large amounts of LDHs[16].

2 Organo-modified LDHs

LDHs have high charge density, which is generally 3- to 4-fold higher than that of layered silicates[30,31]. The high charge density as well as the high content of interlayer anions and water molecules result in strong interlayer electrostatic interactions between sheets and strong hydrophilic properties, and thus prevent both swelling and exfoliation of the LDH sheets. Therefore, in order to facilitate the intercala-

tion of LDHs into polymer matrixes and to reach a good level of dispersion, the interlayer space of LDHs must be chemically modified to eliminate the interaction and obtain the hydrophobic property of LDH layers. Several methods can be applied to prepare organo-modified LDHs, such as ion-exchange, coprecipiation, reconstruction, melt reaction, etc.[32].

2.1 Ion-exchange method

Various organo-modified LDHs can be obtained by incorporating a huge variety of organic anions into the LDH interlayer regions[27,32,33]. When ion-exchange method was applied, the CO_3^{2-} anions should be eliminated, because they have strong interactions with LDH layers and cannot be substituted by other anions. Fortunately, although it is very difficult to completely eliminate the existence of CO_3^{2-} anions, it is feasible that the effect of CO_3^{2-} is limited in such a range that the intercalation of polymer chains cannot be prevented[34].

2.2 Coprecipitation method

Coprecipitation method requires the addition of metal salts solution to a base solution containing the organic anions at a constant pH value. Hsueh et al.[35,36] prepared MgAl-aminobenzoic acid (AB) LDHs by adding MgAl nitrates solution into the AB solution at a constant pH value of 10 controlled by NaOH solution.

2.3 Delamination and reconstruction method—special properties

Another promising way for the preparation of organo-modified LDHs is the delamination-restacking process, which can obtain the exfoliated LDH layers and thus is appropriate for the subsequent dispersion of LDH layers into polymers. Although, as mentioned above, LDHs do not present a natural tendency to exfoliate, recent attempts for delamination of LDH layers were successful.[21,34,37—42]

LDH layers can be calcinated into LDOs. For some LDHs, these LDOs can reconstruct back to the parent LDHs either by cooling in air or soaking in an aqueous solution, which is the so-called memory effect[43]. For example, the LDHs can be obtained by contacting the LDOs with the polystyrene sulfonate (PSS) solution, wherein the LDHs present similarities on crystallinity and morphology to those prepared by direct exchange[4].

3 Synthesis and characterization of polymer/LDH nanocomposites

Polymer/LDH nanocomposites can be synthesized by several methods, as illustrated in Fig. 2[4]. In general, according to the different dispersion states of the LDH layers in the polymer framework, two main types of polymer/LDH nanocomposite, intercalated and/or exfoliated nanocomposites, can be obtained. In the above types of polymer/LDH nanocomposites, the exfoliated ones usually attract more attention because they have nanoscale dispersion of high aspect ratio LDH layers in polymer nanocomposites and thus can give some improved properties compared with micro-dispersed and conventional composites[44].
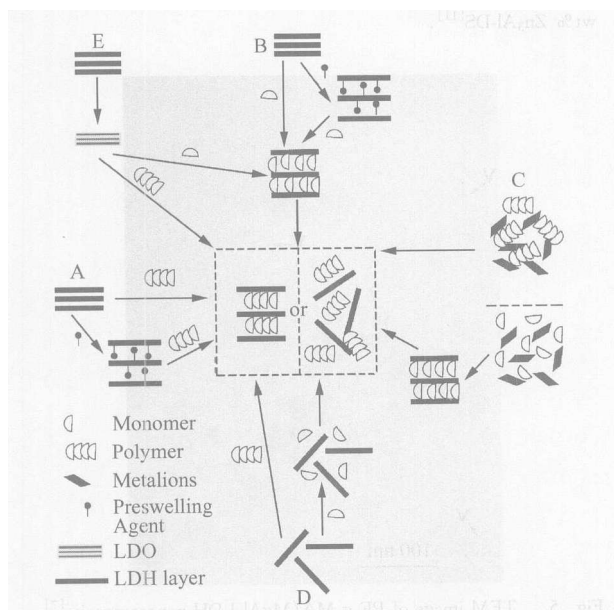

Fig. 2.   Illustration of preparation methods for polymer/LDH nanocomposites. A, direct intercalation; B, *in situ* polymerization; C, *in situ* synthesis; D, exfoliation/restacking; E, reconstruction.

The X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses are generally applied for the characterization of polymer/LDH nanocomposites. The XRD analysis can give useful information on the types of the layered structures, i.e. intercalated and/or exfoliated structures, because the peaks change with the gallery height of the LDHs. However, the XRD results cannot provide a complete picture of the state of the nanocomposites. Moreover, for the exfoliated nanocomposites, LDH layers are often randomly dispersed in the polymer matrixes and the basal spaces are generally larger than 10 nm, which is beyond the range that the XRD can

analyze. Therefore, to obtain the complete information of the materials, actual images, such as TEM images, are required.

3.1 Direct intercalation

Polymer/LDH nanocomposites can be obtained by direct intercalation of polymer chains into organo-modified or pristine LDH layers in solution or melting systems. For example, when the polyethylene-graft-maleic anhydride (PE-g-MA) and the organo-modified Mg3Al-LDH were refluxed in xylene, the exfoliated PE-g-MA/LDH nanocomposites can be obtained[7,8]. And the linear low density polyethylene (LLDPE)/ZnAl-LDH nanocomposites have also been prepared in a non-polar system and characterized by XRD and TEM analyses.[5] Fig. 3 shows the XRD patterns of Zn3Al-DS and LLDPE/ZnAl-LDH composites, which reveals the structural changes of the samples with different LDH loadings. It can be seen that the basal space of the sample with 95% LDH loading (2.45 nm, Fig. 3(b)) reduces in comparison with that of the original Zn3Al-DS powder (2.55 nm, Fig. 3(a)), which suggests that the LLDPE chains are not intercalated into the galleries of the LDH layers in this sample. However, the LLDPE chains in the sample with 50% LDH loading show the expansion of basal space (3.5 nm, Fig. 3(c)), indicating that the LDH layers are partially exfoliated. The diffraction peaks of the Zn3Al-DS component in the samples with 20% (Fig. 3(d)) and 2% (Fig. 3(e)) LDH loading completely disappear, which means that the exfoliated state is obtained when the LDH loading is lower than 20%.
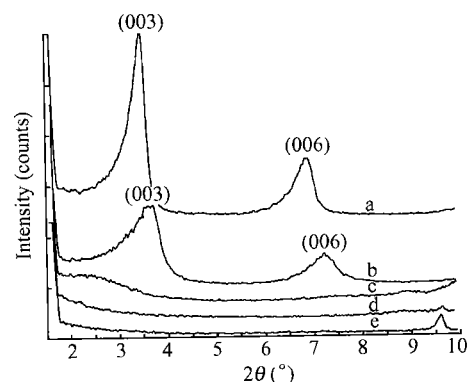

Fig. 3.   XRD patterns of (a) Zn3Al-DS sample and LLDPE/Zn3Al-DS samples with (b) 95%, (c) 50%, (d) 20%, and (e) 2% LDH loadings.[5]

When solution intercalated method is applied, several factors can influence the dispersion state of

LDHs in the nanocomposites. Recently, Qiu et al.[15] studied the influences of LDH loading, refluxing time, LDH concentration in the solution, and preparation method, on the structures of the polystyrene (PS)/ZnAl-LDH composites prepared by solution intercalation. They found that completely exfoliated LDH layers can be achieved by decreasing the content of LDH and elongating the refluxing time. More interestingly, the preparation method also has decisive effect on the structure of the nanocomposite. For example, slow evaporation of the solvent only leads to an intercalated structure, while rapid evaporation is in favor of the exfoliated structures. However, when rapid precipitation of the colloidal suspension in ethanol is applied, the completely exfoliated structures are obtained.

3.2 In situ methods

The incorporation of a polymer between the LDH sheets may be achieved by the in situ methods. For instance, the intercalated PMA/Zn$_3$Al-LDH nanocomposite with 5 wt% LDH was synthesized by in situ bulk polymerization of methyl acrylate (MA) with an organo-modified Zn$_3$Al-DS LDH[11]. Fig. 4 presents the morphology of the obtained nanocomposite, which shows that most of the Zn$_3$Al-DS layers are face-to-face stacked with about 3 nm spacing in the PMA matrix. Combined with the XRD data, it can be seen that the basal space increases and the order of LDH layers is not destroyed in this intercalated nanocomposite. However, it is noteworthy that the TEM images of the exfoliated polymer/LDH nanocomposites are very different from those of exfoliated polymer/layered silicate nanocomposites in which the delaminated silicate layers are often face-face orientated. In the exfoliated polymer/LDH nanocomposite, the LDH sheets are generally dispersed disorderly in the polymer matrixes and mostly parallel to the cutting section of the TEM specimen (Fig. 5)[7]. O'Leary et al. have reported the similar results from exfoliated polyacrylate/LDH nanocomposites.[34]

Because the LDH have no tendency to swell and exfoliate in water, no much work has been done by the in situ emulsion and suspension polymerization methods to synthesize polymer/LDH nanocomposites, although these methods have been proved to be new and efficient for synthesizing the polymer/layered inorganic nanocomposites in recent years[45,46]. Chen et al.[6] reported the in situ suspension synthesis of the
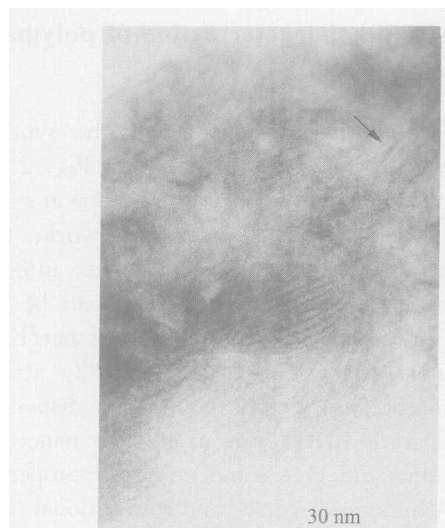

Fig. 4. TEM images of PMA/Zn$_3$Al LDH nanocomposite with 5 wt% Zn$_3$Al-DS[11].
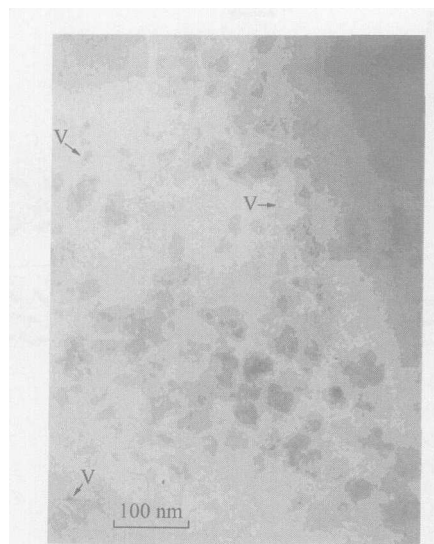

Fig. 5. TEM image of PE-g-MA/MgAl-LDH nanocomposite[7].

PMMA/Mg$_3$Al LDH nanocomposite with high transparency and enhanced thermal property by adding base solution into the emulsion consisting of metal ions, DS, methyl methacrylate (MMA), and initiator, followed by thermal initiation polymerization. Recently, Ding et al.[12] found an effective way for preparing the exfoliated PS/LDH nanocomposites using in situ emulsion polymerization in the presence of reactive surfactants and long-chain spacers, in which the PS/LDH nanocomposites can be completely exfoliated even at the 10 wt% LDH loading.

3.3 Exfoliation/restacking process

The first key factor of the exfoliation/restacking process is to obtain the exfoliated LDH layers in a certain solution system before the polymers or monomers

are introduced. As discussed in Section 2. 3, the preparation of exfoliated LDH is very difficult, thus this method is rarely studied. Hu et al.[47] reported the synthesis of exfoliated nanocomposite based on PMMA and glycine-modified MgAl-LDH via exfoliation/adsorption process using acetone as co-solvent. Using the same method, they also obtained the intercalated poly(vinyl alcohol) (PVA)/LDH nanocomposites.[48]

4   Properties and potential applications of polymer/LDH nanocomposites

4.1   Thermal and flame-retardant properties

Polymer/LDH nanocomposites have unique thermal stability and have been proven to be promising candidates for fire retardants compared with virgin polymers and conventional composites[19,49]. For example, the thermal decomposition temperature of the PE-g-MA/LDH nanocomposite with 5 wt% Mg3Al-DS can be 60 ℃ higher than PE-g-MA when 50% weight loss is selected as a comparison point. And this nanocomposite has a slower thermo-oxidative rate than PE-g-MA in the range of 200 ℃—320 ℃.[7,8]

In general, it has been found that the incorporation of LDH into the polymer matrixes can enhance thermal stability by promoting the charring process of polymer matrixes and acting as a superior insulator and mass transport barrier to the volatile products generated during the decomposition. Chen et al.[5,9] found that the LLDPE/Zn3Al LDH nanocomposites show a faster charring process in the range of 200 ℃—400 ℃ and an enhanced thermal stability at above 370 ℃ than LLDPE. Several studies also reported the higher thermal stability of polymer/LDH nanocomposites than those of the polymer matrixes.[6,34—36,47]

When LDH is used as flame-retardant filler, the polymer/LDH nanocomposites will be embedded into improved barrier properties by hindering diffusion of volatile decomposition products, carbon monoxide and smoke yields. At the same time, dehydration of LDH and promoted char formation during subsequent thermal treatment may also enhance the properties of self-extinguishing flammability. The flame retardancy was improved in the polyamide-6/polypropylene (PP) blends containing LDHs and NH4-polyphosphate[50].

4.2   Mechanical properties

The influence of LDH on the mechanical proper-

ties of the polymer/LDH nanocomposites is complicated. In general, the dispersion of LDH into the polymer matrixes can improve the elasticity, strength, storage modulus and strain at break, while decrease the elongation at break in comparison with the polymer matrixes. For example, Chen et al.[8] found that the tensile strength dramatically increased from 0.46 MPa of PMA matrix to 3.81 MPa of the PMA/Zn3Al-LDH nanocomposite with 5% LDH loading, and the elongation at break was not modified. However, the tensile strength of the microscopical composite based on PMA and Zn3Al-LDH with 5% LDH loading only increased to 2.36 MPa, while the elongation at break decreased from 970% to 630%. They also found that the Yong's modulus of LLDPE/Zn3Al LDH nanocomposite with 20 wt% LDH increased while the strength and elongation at break decreased. This may be caused by the decrease of crystallinity degree of LLDPE matrix and/or some aggregations of exfoliated LDH layers in the LLDPE matrix.[9]

Hsueh et al.[35] reported that the polyimide (PI)/LDH nanocomposites exhibited higher storage moduli and loss moduli compared with those of pure PI. The initial tensile modulus of these nanocomposites increased with the increasing LDH loadings. The maximum tensile strength and elongation were obtained at the 5 wt% and 4 wt% LDH contents, respectively.

4.3   Optical properties

When LDHs are introduced into the polymer matrixes, the transparence of the polymers was often sacrificed. Only several transparent polymer/LDH nanocomposite systems can be obtained.[6,36] Fig. 6 is a photo taken from a 0.5 mm thick sheet of PMMA-MgAl nanocomposite with 33% LDH loading, which indicates the high transparency of the nanocomposite, whereas the PMMA-MgAl micro-

Fig. 6.   Photograph taken from 0.5 mm thickness PMMA/Mg3Al LDH nanocomposite sheet on a graphic pattern by a camera[6](LDH content: 33%).

composite is an opaque white sheet even if its thickness is less than 0.1 mm.

4.4 Polymer electrolyte

Polymer electrolytes may play an important role in the development of safe and transportable energy storage such as lithium polymer rechargeable batteries or direct methanol fuel cell. In this area, poly(ethylene oxide) (PEO) doped with alkali salts is commonly used and, however, suffers a decrease of conductivity due to the increase of crystalline phase of PEO. To overcome the problem, some inorganic fillers were used as substitutes of the alkali salts to inhibit the polymer crystallization, and thus enhance the amorphous PEO phase. Liao et al.[51,52] have found the beneficial role of LDHs materials as polymer electrolytes. Oligo(ethylene oxide) modified LDH material was used as nano-filler in PEO. The conductivity of the nanocomposite sharply increases with the presence of LDH layers. This phenomenon can be explained by the dispersion of LDH, which leads to the stability of amorphous PEO phase and thus making the migration of Li^+ ion more easily inside the nanocomposite. Polymer electrolyte films were also prepared by dispersing LDH materials in poly(ethylene glycol diacrylate) (PEGDA) with $LiCF_3SO_3$ salt[53]. Compared with the virgin polymers, the ionic conductivity as well as the tensile modulus of the PEGDA/LDH system increase.

5 Perspective

As described above, the polymer/LDH materials are proved to be a new emerging class of nanocomposites, and the introduction of LDHs into polymer matrixes brings many useful new properties compared with the conventional materials. However, more simple and environment-friendly methods are still expected, and little research has been devoted to the application of the polymer/LDH system. Due to the highly tunable composition of LDH layers, we believe that diverse polymer/LDH nanocomposites with multi-functions can be obtained, which are suitable for a large variety of applications, such as IR/UV absorbents,[17,54] flame-retardant fillers,[19,49] bio-materials,[20,55] clay-modified electrodes,[51,52] batteries,[56] photochromic materials,[57] catalysts,[16] waste-carriers materials,[58] and so on.

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