## CHAPTER 4

# *Mineral-derived Fire Retardants*

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## 4.1 Inorganic Fire Retardants

## 4.1.1 Introduction

Fire hazard refers to a disaster caused by uncontrolled burning in time or space. Among all kinds of catastrophes, fire is one of the most frequent and universal disasters which threaten public safety and social development. The World Fire Statistics 2019 shows an average of 3.8 million fires per year from 1993 to 2017, resulting in at least 1 million deaths.<sup>1</sup> Due to their excellent chemical and physical properties, polymer materials have found widespread applications in modern human life, especially in architecture, household appliances and automobiles. However, the chemical nature of macro-molecules is organic, making them susceptible to being damaged and/or catching fire if they come into contact with a flame.<sup>2</sup> Hence, polymer

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substances generally contribute to the development of fire behaviour. Besides, during combustion, polymer materials usually produce toxic gases, such as CO, HCl and NH<sub>2</sub>, which cause secondary damage to people in addition to burns.

Therefore, improving the fire retardance of polymers has become a common understanding. Nowadays, the paramount routes applied to improve the fire retardance of polymers are introducing fire-retardant (FR) groups to polymer molecular chains,<sup>3,4</sup> preparing monomers with intrinsic high flame retardancy<sup>5,6</sup> and incorporating flame retardants into the macromolecular substrate. In contrast, adding flame retardants directly to polymers is a relatively simpler process and has a diverse selection of flame retardants, which are mainly divided into organic flame retardants and inorganic flame retardants. Organic flame retardants principally involve halogens, nitrogen, phosphorus, silicon, etc. Although organic fire retardants can impart polymer materials with high flame retardance, some of them also have some obvious disadvantages such as high cost, poor smoke control effect and production of corrosive and toxic substances,<sup>7,8</sup> which may cause secondary pollution to the environment. In contrast, inorganic flame retardants usually have good stability, are acid-free, are environmentally friendly and are of low price.

From the perspective of safety and environmental protection, inorganic flame retardants have become an inevitable trend. So far, various inorganic fire retardants have been developed, such as metal oxides (MeO),<sup>9</sup> metal hydroxides<sup>10</sup> and metal carbonates.<sup>11</sup> More importantly, the outstanding fire extinguishing performance of inorganic flame retardants both in the gas phase, releasing water vapor (a lot of heat is absorbed in the gas-liquid transition) or CO<sub>2</sub>, which both dilute the pyrolysis products, and in the condensed phase, generating MeOs to increase the char yield and then MeO-char layer formed on the surface of the substrate, acts as to inhibit the migration of mass/oxygen/heat.<sup>12–14</sup> Consequently, the FR behaviours of the polymer composite are obviously improved, including increments in the limiting oxygen index (LOI) and the vertical combustion (UL-94) rating.

Although flame retardant research has been a subject of interest for more than a century, this old domain is experiencing a renaissance due to the recent strong societal interest in green materials and approaches that are beneficial for human health.<sup>15</sup> Because of their unique strengths, inorganic retardants draw widespread attention from the industry and academic sections. Hence, in recent years, the field of inorganic flame retardants has developed significantly. In the past decade, the number of papers that have reported on inorganic flame retardants has also been increasing. This review article, thus, will introduce the characteristics, preparation and application of several metal compounds and further discuss the effects of modified inorganic fire retardants and the multiple flame retardants system on the enhancement of the FR performance of the polymer composites.

# 4.1.2 Aluminum Hydroxide as an Inorganic Fire Retardant in Composites

#### 4.1.2.1 Characteristics of Aluminum Hydroxide

Aluminum tri-hydroxide (ATH) is a sort of amphoteric hydroxide, which can react with acids to form salt and water and with strong bases to form salt and water. Due to its acidity, it can also be called aluminic acid ( $H_3AlO_3$ ). In addition, while reacting with a base, ATH forms a tetrahydroxy aluminate ([Al(OH)<sub>4</sub>]<sup>-</sup>); hence, it is usually regarded as monohydrate metaluminic acid (HAlO<sub>2</sub>·H<sub>2</sub>O). ATH is usually used in halogen-free FR insulating or cable sheathing materials, showing good behaviour, particularly in suppressing smoke.<sup>16–18</sup> Besides, ATH is nontoxic and of low price. In view of the above advantages, ATH is the largest and most widely used inorganic FR additive, and its use is increasing year by year.

However, the ATH FR efficiency is low. In order to improve the FR properties of polymer composites, more than 40–70 wt% ATH is incorporated to meet the requirement of different products in flame retardancy,<sup>19</sup> which results in deterioration of the mechanical properties of the end products dramatically.<sup>20</sup> Hence, the other fire retardants are utilized to constitute an FR system with ATH which reduces the dosage of ATH. Besides that, because of its poor thermal stability, ATH undergoes endothermic decomposition at 180–200 °C, which restricts the processing temperature heavily. Therefore, there are not so many species of polymer that could use ATH as a fire retardant. Most of them are polymers with a low viscosity temperature, such as ethylenevinyl acetate (EVA),<sup>21–23</sup> linear low-density polyethylene (LDPE)<sup>18</sup> and polypropylene (PP).<sup>24,25</sup>

## 4.1.2.2 Preparation of Aluminum Hydroxide

The preparation methods of ATH are divided into physical and chemical approaches. The physical method usually refers to the mechanical disruption to ATH with a large particle size, *i.e.*, the non-industrial grade ATH is washed, dried and processed into ATH powder by airflow mill or ball mill. The ATH powder produced by this means is irregularly shaped with a size of  $5-15 \mu m$  and wide particle size distribution. When the as-prepared ATH powder is applied in the manufacture of wires and cables, its processing performance is poor, and the end product has poor fire retardance. Therefore, the general industrial production of ATH powder is using a chemical process, which yields products of stable quality, high purity, fine particle size, and narrow particle size distribution. Among them, chemical methods mainly include the precipitation method, carbonation method, organic aluminum hydrolysis method and sol–gel method.

The precipitation method involves direct precipitation and homogeneous precipitation approaches. The direct precipitation method is that incorporating the precipitant into the aluminate solution to give an ATH powder with high purity under certain conditions. In contrast, the added precipitant does not react with the precipitated fraction immediately in the homogeneous method. This route refers to adopting a chemical reaction that makes the crystalline ions be released slowly in the solution and the precipitation in the solution is guaranteed to be in a state of equilibrium *via* control of the concentration of precipitation, so as to deposit evenly. In the study of Ferhat Kara and Sahin,<sup>26</sup> urea and aluminum nitrate solution were employed as the raw materials to fabricate ATH, and their study indicated that the concentration of the aluminum nitrate solution has a direct bearing on the particle size dispersion and agglomeration degree of products.

The organic aluminum hydrolysis method means that isopropyl aluminum is hydrolyzed in an  $NH_3 \cdot H_2O$  system under the action of a certain catalyst, and the resulting precipitation is filtered and dried to obtain ATH particles with an average particle size of 90 nm. The strengths of this method are simple operation, small particle size and narrow particle distribution, but the disadvantages are serious sample agglomeration and the high cost of organic raw materials.

Another good technique for synthesizing ATH is the sol-gel method, which normally obtains ATH powder *via* dry grinding of its gels. ATH gels are prepared through the transformation of the ATH colloids, which are the outcomes of the hydrolysis of aluminum compounds under the conditions of a certain water bath temperature, stirring rate and pH value. Compared with the precipitation method, the sol-gel method has the advantages of low temperature, simple equipment and being a controllable process. It also avoids the anionic pollution caused by inorganic salts in the precipitation method, but the sol-gel method also has the problems of high cost and environmental pollution.

More methods available for obtaining ATH include the carbonation process which is used to prepare alumina hydroxide powder by passing  $CO_2$  into sodium aluminate solution and controlling the reaction conditions, such as  $CO_2$  ventilation rate, decomposition temperature and pH value. However, Liu *et al.*<sup>27</sup> found that the carbonation decomposition of potassium aluminate solution is more available compared with the carbonation decomposition of sodium aluminate solution *via* the investigation of the carbonation process of potassium aluminate.

## 4.1.2.3 Application of ATH Composites as Flame-resistant Materials

In the choice of other flame retardants to form the FR system with ATH, researchers are inclined to select the fire retardants, which simultaneously act as synergistic agents to ATH as well, in order to decrease the dosage of ATH powder further.

Ai *et al.*<sup>28</sup> adopted hexakis-(4-boronic acid-phenoxy)-cyclophosphazene (CP-6B) (the structure of CP-6B is shown in Figure 4.1) and ATH to constitute a flame-retardant system and it was added into high density polyethylene (HDPE) to obtain a composite, *i.e.*, HDPE/ATH/CP-6B. ATH/CP-6B decomposed



CP-6B

**Figure 4.1** Chemical structure of CP-6B.<sup>28</sup> Reproduced from ref. 28 with permission from Springer Nature, Copyright 2021.

nonflammable gases and formed a dense layer on the surface of the composite. The FR behaviour of PE/20%ATH/20%CP-6B is better than that of PE/40%ATH, demonstrating that there is a synergistic effect between ATH and CP-6B. Zeng *et al.*<sup>29</sup> formed a binary FR system composed of ATH and ammonium polyphosphate (APP) and incorporated it into polyurethane (PU) to obtain the composite PU/ATH/APP. In comparison with virgin PU, PU/20%APP and PU/20%ATH samples, the composite PU/15%APP/5%ATH had a higher thermal stability, more residual carbon, a more complete and dense carbon layer and better fire retardance, demonstrating that a synergistic interaction exists between them.

In addition to that the FR systems consisting of organic fire retardants and ATH show good performance in enhancing the FR behaviours of a polymer matrix, and some inorganic fire retardants can also achieve such an effect. Xu *et al.*<sup>30</sup> utilized inorganic fire retardants, including expanded graphite (EG), red phosphorus (RP), zinc borate (ZnB) and magnesium hydroxide (MH), to constitute an FR system, and they were added into HDPE to give a series of composites. With the incorporation of RP and EG, the ATH flame retarded HDPE composites show obvious synergistic effects in improving the flame retardancy. Nevertheless, there are no synergistic effects between ATH and MH, and ATH combined with zinc borate has antagonistic effects indeed.

In general, to overcome the shortcoming of high loading of ATH, ATH should be added into the polymer substrate as a single element of the FR system to greatly improve the FR performance and maximize the retention of the mechanical properties of the polymer. Besides, what can be seen is that other types of flame retardants do not necessarily have synergisms with ATH and even have some antagonistic effects, which is obviously contrary to our purpose. Hence, more flame retardants that have strong synergistic interactions with ATH need to be developed.

# 4.1.3 Magnesium Hydroxide as an Inorganic Fire Retardant in Polymers

#### 4.1.3.1 Characteristics of Aluminum Hydroxide

Similar to ATH, magnesium hydroxide (MH) as well is a kind of halogen-free fire retardant. However, MH possesses higher thermal stabilities, and its endothermic decomposition temperature is 340-490 °C, which is nearly 100 °C higher than that of ATH. So, it can be applied as a fire retardant to polymer materials with relatively high processing temperatures, such as polyethylene terephthalate (PET)<sup>31</sup> and acrylonitrile-butadiene-styrene (ABS).<sup>32</sup> In particular, MH is one of the most eco-friendly fire retardants, which only produces water vapor during combustion. Except for inhibition of polymer ignition, MH also can be regarded as a smoke suppressor.<sup>33-35</sup> Due to its rich resources, comparatively higher decomposition temperature, hypotoxicity and heat insulation effects,<sup>36-40</sup> it is widely used in applications of the industry. Although MH and ATH have the same FR mechanism, the decomposition of MH can generate more steam in the situation of the same quality of loading, which indicates more heat can be carried out.

However, it is still a flame retardant with low flame efficiency, like ATH and layered double hydroxide (LDH) resulting in high loading of MH in the polymer matrix. Hence, many researches reduced the dosage of MH *via* the modification of MH and/or the synergistic effects generated from remixing it with other additives with inherent fire retardance. Thus, the application examples of magnesium hydroxide as a flame retardant described in this chapter involve the modification of magnesium hydroxide and the FR system composed of MH and other fire retardants.

## 4.1.3.2 Preparation of Magnesium Hydroxide

The good distribution of MH in polymer substrates is conducive to the enhancement of the FR performance of the polymer composites.<sup>41</sup> Therefore, it is of great importance to synthesize MH particles with small particle sizes and narrow particle size dispersion. The fabrications of MH mainly include direct precipitation, magnesium oxide hydration and electrochemical and hydrothermal crystallization. Moreover, structure-directing agents are of benefit to the preparation of MH particles with good dispersion.

The direct precipitation process refers to incorporating a certain amount of alkaline precipitating agents such as urea, sodium hydroxide and ammonia into a solution containing  $Mg^{2+}$ , which forms the white deposition of  $Mg(OH)_2$  separating from the solution. Using the cationic surfactant cetyltrimethylammonium bromide (CTAB) as a crystal modifying agent, An *et al.*<sup>42</sup> took MgCl·6H<sub>2</sub>O and ammonia as raw materials to give MH particles with polygon morphology and good distribution at room temperature. Jiang *et al.*<sup>43</sup> fabricated layered MH particles by using MgCl·6H<sub>2</sub>O and NaOH as raw materials and urea and C<sub>2</sub>H<sub>5</sub>OH as secondary additives. When C<sub>2</sub>H<sub>5</sub>OH is added into the reactive system, MH with the morphology with an almost hexagonal sheet is obtained, demonstrating that C<sub>2</sub>H<sub>5</sub>OH plays a role in regulating the form of MH. Nevertheless, with the addition of urea, high purity ATH particles are prepared.

The magnesium oxide hydration approach involves the hydration reaction of magnesium oxide, which means that MH precipitates are gradually formed when magnesium oxide is dissolved in water. In spite of the process of magnesium oxide hydration being a simple precipitation reaction, several variables should be elaboratively controlled during the reaction so as to give the desired MH particles.<sup>44</sup> Otherwise, the application of MH will be restricted by some problems which easily occur, such as a low rate of hydration, agglomeration and bad morphology.<sup>45,46</sup>

The electrochemical process is conducted by electrolysis of magnesium aqueous solution or molten salt. Zou *et al.*<sup>47</sup> synthesized highly textual lamellar mesostructured Mg(OH)<sub>2</sub> thin films *via* one-step cathodic reduction of magnesium nitrate bath at ambient temperature. Cvetković *et al.*<sup>48</sup> reported a novel method based on the electrolysis of the molten magnesium nitrate hexahydrate enabling the simultaneous formation of magnesium oxide and hydroxide which possess a flower-like, honeycomb-like structure. Despite that products with special structures can be prepared, side reactions are prone to occur leading to low product purity, and its production cost is relatively high.<sup>49</sup>

More methods are available for synthesizing more suitable MH. This type of method is hydrothermal crystallization, which refers to the reaction between the solution containing  $Mg^{2+}$  and alkaline solvent in a closed container under a high temperature and pressure. In Dhaouadi *et al.*'s report,<sup>50</sup> rod-like virgin MH with a diameter of about 10–40 nm and a length of up to 300 nm was synthesized from the raw material MgO, using hydrothermal treatment in the presence of a surfactant as a template agent (CTAB). Adopting MgCl·6H<sub>2</sub>O as a raw material, Fang *et al.*<sup>51</sup> incorporated polyvinylpyrrolidone (PVP) into the system (using the hydrothermal method at 180 °C and heat preservation for 5 h) to give MH with an average particle size of 174 nm. The results show that PVP decreases the particle size of MH but hinders the growth of the crystal.

## 4.1.3.3 Application of MH Composites as Flame-resistant Materials

Despite its outstanding performance, the polarity and hydrophilic properties of MH give rise to poor compatibility with the polymer matrix, which results in the easy formation of aggregates and serious destruction of the mechanical behaviours of the polymer composites ulteriorly. To improve its compatibility with the polymer substrate, the route of surface modification to MH has been developed, and modifiers principally consist of a silane coupling agent,<sup>52</sup> a titanate coupling agent<sup>53</sup> and a saturated or unsaturated higher fatty acid salts.<sup>54,55</sup> This allows modified particles to be more hydrophilic,<sup>56</sup> and then MH particles have a good distribution in the polymer substrate.



**Figure 4.2** The structural representation of  $eTi_{4000}$ .<sup>53</sup> Reproduced from ref. 53 with permission from Elsevier, Copyright 2018.



**Figure 4.3** Reaction schemes of the MH-silane coupling agent and MCA.<sup>52</sup> Reproduced from ref. 52 with permission from Springer Nature, Copyright 2020.

Lu et al.<sup>53</sup> fabricated composites through the surface modification of MH with a polyether titanate coupling agent ( $eTi_{4000}$ , shown in Figure 4.2) and incorporated it into PVC to give a composite with enhanced FR performance. In addition, the steric hindrance from macromolecular grafting is a partial reason that reduces the agglomeration of MH in the polymer matrix, which improves the flame retardance of the composite as well. The modified MH can constitute a flame-retardant system with other types of additives with intrinsic fire retardance by means of the formation of hydrogen bonds. In Zheng et al.'s study,<sup>52</sup> functionalized MH was prepared via the surface modification using  $\gamma$ -(2,3-epoxypropoxy)propyl trimethoxysilane (KH-560), it was encapsulated by melamine cyanurate (MCA) (the process is shown in Figure 4.3), and eventually, MCA-MH was synthesized. Utilizing PA6 as a polymer substrate, the composite called PA6/MCA-MH was prepared. With a content of 70 wt% MCA-MH, this composite shows excellent fire-retardant performance, which has an LOI value of 32.5 and a UL-94 grade of V-0. Not only can the enhancement of flame retardance be attributed to the uniform dispersion of MH particles, but also is related to a synergistic effect between the two fire retardants.

Besides, for the reason that modified inorganic particles contain reactive functional groups, they can undergo a polymerization reaction with organic monomers and become copolymerization units of polymer molecular chains. Li *et al.*<sup>57</sup> carried out surface modification of MH with phenyl phosphonic acid (PPOA) to give an inorganic–organic monomer (MH-PPOA, the synthesis process is shown in Figure 4.4) with inherent flame retardance. MH-PPOA was incorporated into the backbone of polyethylene terephthalate (PET) to obtain



Figure 4.4 Synthesis of MH-PPOA.<sup>57</sup> Reproduced from ref. 57 with permission from Elsevier, Copyright 2022.



**Figure 4.5** Synthesis of MH-PPOA<sub>*n*</sub>-*co*-PET.<sup>57</sup> Reproduced from ref. 57 with permission from Elsevier, Copyright 2022.

a co-polyester composite (MH-PPOA-*co*-PET) (the synthesis process is shown in Figure 4.5). With the increase of the MH-PPOA monomer content, the LOI value of the composite increases continuously. While the content of the monomer is 7 wt%, the co-polyester attained an LOI of 28.6% and a V-0 grade in the UL-94 test.

The surface modification of MH is indispensable for the inhibition of particle agglomeration. Such modification enhances the interfacial interaction between the MH particles and a polymer matrix leading to a high performance composite material with high fire retardance and a low content of inorganic filler. The prospects of MH particles are attractive. A substantial amount of work still needs to be carried out for the modification of MH.

# 4.1.4 Anhydrous Magnesium Carbonate as an Inorganic Fire Retardant

#### 4.1.4.1 Characteristics of Anhydrous Magnesium Carbonate

Anhydrous magnesium carbonate (AMC), a kind of white crystalline powder, one of the major components of dolomite, is also known as light magnesium carbonate. As a natural mineral, the formation and properties of AMC have been investigated for a long time. However, due to the highly hydrated nature of  $Mg^{2+}$  in solution,<sup>58</sup> it allows the existence of many different forms of hydrated or basic carbonates in the system of Mg-carbonate, which seldom gives rise to reports about the preparation of high purity AMC ulteriorly. However, previously, for the reason that the final product has a low value, the industrial process of AMC cannot attract much attention. In most

instances, AMC is substituted by natural substances or other minerals such as calcium carbonate.  $^{\rm 59}$ 

Nevertheless, with the fast development of inorganic fillers, AMC, as a novel inorganic flame retardant, has attracted more and more attention. The characteristics of AMC are as follows: the decomposition temperature is between 300 and 500 °C, which is close to that of MH and higher than that of ATH; compared with MH and ATH, AMC absorbs more heat and its decomposition rate is higher; AMC has a high  $CO_2$  storage capacity and can generate a large amount of  $CO_2$  during the decomposition course. Beyond that, different from the water vapor released by metal hydroxides,  $CO_2$  is more inclined to sink to the surface leading to the formation of a gas film which isolates the contact between the surface and combustible gases. Likewise, AMC has the same shortcomings as general inorganic fire retardants, such as a low fire-retardant efficiency, low compatibility with the polymer substrate, high dosages and so on.

#### 4.1.4.2 Preparation of Anhydrous Magnesium Carbonate

Due to the harsh synthesis conditions, nowadays, AMCs with high quality are not yet commercially available for mass production.<sup>60</sup> The laboratory preparation of AMC particles also usually needs to be done *via* complicated and lengthy procedures in a strict environment, such as a high temperature (>300 °C), a high CO<sub>2</sub> partial pressure and/or a long process time (>12 h).<sup>61,62</sup> The end products possess an inhomogeneous size and irregular morphology.<sup>63</sup>

Although there are certain difficulties existing in the preparation of AMC with uniform particle size dispersion and small grain size, some progress has been made throughout the world. Xing *et al.*<sup>64</sup> utilized urea as a carbon source and MgCl<sub>2</sub>, MgSO<sub>4</sub>, Mg(OH)<sub>2</sub>, MgO, *etc.*, as magnesium sources, *via* a hydrothermal reaction for 30 h at 160 °C in an autoclave, to obtain rhomboid AMC microcrystalline particles with a particle size of 1–10 µm. Dong *et al.*<sup>65</sup> adopted MH as a starting material to give layered AMC under continuous CO<sub>2</sub> bubbling (0.3–0.7 MPa) at 120–150 °C for 6 h. They found that the regular cubic AM with side lengths of 2–4 µm was fabricated with the incorporation of potassium citrate and the high concentration of K<sup>+</sup> contributed to the synthesis of AMC. In Li *et al.*'s report,<sup>66</sup> the deep eutectic solvent of MgCl<sub>2</sub>·6H<sub>2</sub>O/urea was used as a precursor to synthesize AMC by the hydrothermal process, and single crystals of a layered spiral-type AMC microcube with a grain size of 2–4 µm were obtained. Nevertheless, these procedures still are complex and are carried out under harsh conditions.

Therefore, an approach that can be utilized in the synthesis of AMC particles with suitable particle sizes is introduced in this chapter. Zhao *et al.*<sup>67</sup> used urea as a carbon source and MgSO<sub>4</sub> as a magnesium source through the hydrothermal process for 3 h at 180 °C, and AMC with a small particle size with block-, cube-, corncob- and sphere-like morphologies is fabricated. Chai *et al.*<sup>68</sup> adopted urea, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>HCO<sub>3</sub> as carbon sources and MgCl<sub>2</sub> and MgSO<sub>4</sub> as magnesium sources *via* the hydrothermal process for 3 h at 180 °C in or without the presence of a mineralizer (NaOH, KOH, H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, HAc, NaCl, Na<sub>2</sub>SO<sub>4</sub>, KCl or K<sub>2</sub>SO<sub>4</sub>), and then AMC particles with different morphologies and grain sizes were obtained. In addition, they found that the particle size and morphology of AMC prepared using MgCl<sub>2</sub> as a magnesium source can be better controlled by using the NaOH mineralizer, and the average particle size is  $2-4 \mu m$ , while that of AMC prepared using MgSO<sub>4</sub> as a magnesium source can be better controlled by using the KOH mineralizer, and the average particle size is  $4-6 \mu m$ .<sup>68</sup>

#### 4.1.4.3 Applications of AMC Composites

During the process of preparing polymer composites containing AMC as a fire retardant, the surface modification of AMC should be carried out to strengthen the compatibility between AMC and a polymer substrate. Bi *et al.*<sup>69</sup> reported that AMC with cubic morphology was modified by  $\beta$ -cyclodextrin (CD), which improves its interfacial adhesion to the PVC matrix. With the addition of the modified AMC, the fire-retardant performance of the composite is better than that of virgin PVC. In addition, the THR of PVC composites with a CD@MC mass fraction of 12 wt% was reduced by 51.3% compared with that of pure PVC, indicating the synergistic effect between CD and MgCO<sub>3</sub> in the improvement of the flame retardance of the composites.

For the reason that there are some difficulties in the preparation of AMC, few people can synthesize AMC with an appropriate grain size and morphology for use as a fire retardant. Hence, the utilization of AMC in inorganic flame retardants is limited. It is high time to develop the synthesis and application of AMC.

## 4.1.5 Layered Double Hydroxides as Inorganic Fire Retardants in Composites

## 4.1.5.1 Structure of Layered Double Hydroxides

Layered double hydroxides (LDH), also termed hydrotalcite-like materials or anionic clays, are a typical class of substances easily obtained from both nature and the laboratory.<sup>70</sup> LDHs containing both divalent and trivalent metal ions have been extensively investigated, and the general chemical formula of LDHs is  $[M_{1-}^{II} M^{III}(OH)_2]^{x+}(A^{n-})_{x/n}yH_2O$ , where  $M^{II}$  stands for divalent metal ions such as  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$  and so forth;  $M^{III}$  stands for trivalent metal ions such as  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$  and so forth;  $A^{n-}$  stands for an anion occupying the interlamellar area such as  $Cl^-$ ,  $CO_3^{2-}$ ,  $NO_3^-$  and so forth. Although the scope of *x* is wide and the structure of LDH can be formed, the pure phase of LDH can be acquired in the limited range of  $0.2 \le x \le 0.33$ .<sup>71</sup>

The structure of LDH compounds can be described as follows: (1) consisting of layers with a brucite-like structure carrying a net positive charge, due to the partial replacement of trivalent octahedrally coordinated cations for the divalent cations;<sup>72</sup> (2) for neutralizing the positive charge, anions are intercalated between the layers, forming a basal spacing of less than 2 nm; and (3) for stabilizing the crystalline structure, water molecules share the interlamellar region with the anions.

The application of LDHs has spread into various domains, among which increasing interest comes from the FR materials.<sup>73–75</sup> Being a promising type of inorganic fire retardants, LDHs not only have a stratified structure, but also have the ability to control the structure *via* the variation of the cations and intercalated anions.<sup>76,77</sup> The interlamellar anions can be substituted by other anions which have large steric hindrance *via* the interlayer modification,<sup>78</sup> resulting in the spacing further being expanded. This allows the intercalation of large polymer chains or segments of the chain into their gallery space to be possible, which enhances its compatibility with the polymer substrate. The chemical material used in interlamellar modification can be chosen from a variety of organic and inorganic substances, such as anionic surfactants, polyoxometalate anions and organic metal complex anions. Thus, this review enumerates several modifying agents applied in the modification of LDHs and their effect on the enhancement of fire retardance of the composites.

#### 4.1.5.2 Synthesis of LDH

In spite of the various routes of LDH synthesis, nearly all preparative methods used evolved from the themes of precipitation by base and selective displacement of anions from precursors.<sup>70</sup> The most frequently used approaches comprise coprecipitation, homogeneous precipitation, hydro-thermal crystallization and an ion exchange method.

The coprecipitation method requires adding a salt solution of selected pairs of metal ions to a diluted solution of NaOH and/or NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> or NH<sub>4</sub>OH, and precipitation is obtained. The pH of the above solution is carefully controlled within a constant range of 8 to  $10.^{79}$  By means of hydrothermal treatment of the suspension, samples with a good crystalline structure are usually obtained. Detailed descriptions can be found in many literature reports.

The homogeneous precipitation method which usually adopts "urea hydrolysis" can be used to prepare LDHs with high crystallinity and narrow particle size distribution.<sup>80,81</sup> Mostly, an aqueous solution of needed metal ions in the appropriate molar ratio is heated in the temperature scope from 90 °C to reflux temperature for a time period of 23–24 h. For the reason that ammonium carbonate is produced by the decomposition of urea molecules, the precipitate of LDHs containing  $CO_3^{2-}$  as the intercalating anion is generated in the end.

The hydro-thermal crystallization method refers to the crystallization of an amorphous trivalent metal oxide  $(M_2^{III}O_3)$  precursor in the presence of a suitable divalent metal oxide  $(M^{II}O)$ , with the latter acting as a crystallizing

agent.<sup>82</sup> Obviously, the amorphous hydrated oxide of the LDH trivalent metal component is the precursor  $M_2^{\rm III}O_3$ , whereas the reactive basic oxide of the LDH divalent metal component is the crystallizing agent  $M^{\rm II}O$ . From a practical perspective, the synthesis is actually carried out by hydrothermal treatment of aqueous suspensions of the two metal oxides, and it is completed in a pressurized vessel within a few days.

In the ion exchange method, the interlamellar anions are substituted by other anions. LDHs containing different kinds of anions can be prepared in a particle route through this method. However, the affinity of the anions to such an exchange reaction relies on their electric charge and size completely. Original LDHs disperse in the desired aqueous solution of the required anionic species, and the dispersion is stirred for several hours at room temperature to obtain the desired products.

#### 4.1.5.3 Applications of LDH Composites

Among the numerous reports about modified LDH-based polymer composites, the vast majority of the modifiers are anionic surfactants, especially sodium dodecyl sulfate (SDS). This is because the anionic surfactants are readily available and are of low prices. Shen *et al.*<sup>83</sup> used the coprecipitation method to prepare dodecyl sulfate intercalated CaMgAl-LDHs, and they were added into the intumescent flame retardant (IFR) polypropylene (PP) to give a composite PP/IFR/m-LDHa. m-LDHa has a spacing of 1.76 nm, which is far larger than that of the unmodified CaMgAL-LDH. This allows the distribution of m-LDHa to be more homogeneous in the polymer substrate and further enhances the fire retardance of the PP/IFR/m-LDHa system. When the addition of IFR is 23 wt% and the addition of m-LDHa is 2 wt%, this system has an LOI of 31.5% and the UL-94 rating can be stabilized at V-0 levels. Adopting the coprecipitation method, Ding *et al.*<sup>84</sup> fabricated sodium phenyl phosphate intercalated CuAl-LDH (m-LDHb) and SDS intercalated CuAl-LDH (m-LDHc) and added them into the epoxy (EP) resin to obtain the composites EP/m-LDHb and EP/m-LDHc, respectively. The X-ray diffraction (XRD) patterns of them show that the gallery spacing of m-LDHb is larger than that of m-LDHc, which indicates that the distribution m-LDHbs in the epoxy resin is more uniform. This causes the fire retardance of EP/m-LDHb to be better than that of EP/m-LDHc, and the subsequent CCT test results also exactly verified this point. Wu et al.<sup>85</sup> obtained the lignin-based surfactant sodium lignosulfonate (SLS) intercalated AlMg-LDH (LDH-LS) via the coprecipitation method and added it into polypropylene to give a composite PP/LDH-LS (the process of synthesis is shown in Figure 4.6). The FR performance of this composite is significantly improved, which is mainly attributed to the modification of LS to LDHs making it spread more evenly in the polymer matrix and the synergistic effect between LS and LDHs: the carbon residue and the metal oxides generated by the thermal decomposition of LS and LDHs can form a dense and continuous carbon layer to prevent the diffusion of oxygen and heat.



**Figure 4.6** Schematic diagram of the LDH-LS flame retardant and PP/LDH-LS composite materials synthesized.<sup>85</sup> Reproduced from ref. 85 with permission from Elsevier, Copyright 2021.

The spacing also can be enlarged through the interlayer modification of polyoxometalate anions to achieve the purpose of enhancing the dispersion of LDHs in the polymer matrix. Zhang *et al.*<sup>86</sup> obtained sodium phosphomolybdate hydrate (Na<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] xH<sub>2</sub>O, MoP) intercalated FeMg-LDH (LDH-MoP) and added it into the EP resin to prepare the composite EP/LDH-MoP. The XRD pattern of LDH-MoP shows that the layer spacing is 0.98 nm, which is more than twice that of the original layer spacing. The CCT results show that a small amount of LDH-MoP is introduced into the polymer, and the FR properties of the composite are enhanced obviously. Xu et al.<sup>87</sup> prepared a hybrid (RGO-LDH) of MgAL-LDH loaded graphene via the coprecipitation method, and then CuMoO<sub>4</sub> was used in the interlamellar modification of RGO-LDH to obtain RGO-LDH/CuMoO<sub>4</sub>, with its synthesis process shown in Figure 4.7, eventually, it was added into the EP resin to give a composite EP/RGO-LDH/CuMoO<sub>4</sub>. The addition of CuMoO<sub>4</sub> not only can expand the spacing, but also its decomposition products MoO<sub>3</sub> and Cu<sub>2</sub>O are beneficial for the formation of carbon layers and an increase in the density of carbon layers.

The organic acid with inherent fire retardance used in the interlayer modification can play a "1 + 1 > 2" effect. Zhang *et al.*<sup>78</sup> adopted 2-carboxy ethyl(phenyl)phosphinic acid (CEPPA) as an FR modifying agent to MgAl-LDH to obtain modified LDH (CLDH) and added it into the intumescent flame retardant (IFR) polyethylene to give the composite PP/IFR/CLDH.



**Figure 4.7** Illustration of the CuMoO<sub>4</sub> modification of RGO-LDH.<sup>87</sup> Reproduced from ref. 87 with permission from Elsevier, Copyright 2017.

The CEPPA intercalating on the surface of MgAl-LDH makes the spacing be enlarged to 1.26 nm, which improves the distribution of LDHs in the polymer matrix. Besides, the endothermic decomposition of CEPPA can take away a lot of heat, and its decomposition products absorbing on the carbon layer and the metal oxide form a dense carbon layer which insulates the transition of heat and air. This allows the FR behaviours of the composite to be enhanced. Using the coprecipitation method, Wang *et al.*<sup>88</sup> prepared the phytic acid (Ph) intercalated MgAl-LDH (Ph–LDH) and added it into the intumescent flame retardant (ammonium polyphosphate, APP) PP to obtain the composite PP/APP/Ph–LDH. There are analogous synergistic effects between Ph and LDH, which improves the fire retardance of the composites.

The interlamellar modification of LDH is necessary to be carried out, which makes the original spacing be expanded by nearly two times which is conducive to the intercalation of polymer molecular chains to improve the compatibility of LDH with the polymer matrix. Although the types of modifiers tend to be diversified, the modifying agents with intrinsic fire retardance are the first choices, such as phosphorus-based fire retardants and polyoxometalate anions. Those kinds of flame retardants can not only improve the distribution of LDH, but also improve the FR efficiency of modified LDH through synergistic effect with LDH.

#### 4.1.6 Conclusions

Inorganic fire retardants have been discussed in this chapter, and the characteristics, preparation and application of ATH, MH, AMC and LDH are specified in detail. Several advantages of inorganic fire retardants, being the

reasons why halogen fire retardants are gradually being replaced, have been highlighted. However, it is noteworthy that problems inherent in inorganic flame retardants remain stumbling blocks.

But there are still some paths to overcome the issues of the metal compound fire retardants. The agglomeration of inorganic particles is effectively alleviated by surface modification of inorganic flame retardants, which also indicates the possibility of addressing dispersion problems associated with traditional inorganic fillers such as metal hydroxides. The problem of their high content in the polymer matrix which is caused by the low efficiency of inorganic flame retardants can be solved by the synergism among inorganic flame retardants and other fire retardants. Some researchers creatively utilized modifying agents with fire retardance to solve the two problems with a substance, which provided the train of thought for the development of inorganic flame retardants. The synthesis of new modifiers with good flame retardancy plays a crucial role in dealing with the long-term problems caused by the shortcomings of inorganic flame retardants.

## 4.2 Nanoscale Clays

#### 4.2.1 Introduction

Nanoclays are defined as layered mineral phyllosilicates with more than one dimension at the nanoscale, such as montmorillonite (MMT), hydrotalcite (layered double hydroxide, *i.e.*, LDH), halloysite (HNT), sepiolite, palygorskite, *etc.* The addition of nanoclays into polymeric materials brings about multifunctional reinforcement, depending on the physiochemical characteristics and dispersion state of nanoclays. The pioneering researchers conducted massive works to reveal how and why the nanoclays influenced the fire retardancy of polymers.<sup>89</sup> Anyhow, the lab-scale synthesis and modification of nanoclays favour the improvement of fire retardancy based on various mechanisms. The intercalation modification of lamellar nanoclay and hierarchical construction of nanoclay represent the main developing trend towards better fire retardancy. For example, compared with the naturally occurring LDH, the direct inorganic assembly of LDH features a convenient selection of appropriate constituting elements for targeted fire retardancy.

The incorporation of nanoscale clay into polymeric materials is subject to either melt or solution blending. The dispersion state of nanoclay in polymeric materials acts as the most critical parameter to determine the ultimate property. The lamellar nanoclay presents three typical dispersion states in the polymer matrix, *i.e.*, pristine, intercalated and exfoliated states (see Figure 4.8a and b).<sup>90</sup> Theoretically, a higher degree of exfoliation promotes the nanodispersion of nanoclays and optimizes the multifunctionality of polymers, *i.e.*, mechanical property, barrier effect and fire retardancy. The parameters for regulating the dispersion of nanoclay are the coupled effect from delaminating kinetics and thermodynamics. From a material perspective, the thermodynamics pertaining to the interfacial compatibility between nanoclay





lamellas and a polymer governs the ultimate dispersion state. In the melting processing, the nanoclay-compatible reactive intercalators (*e.g.*, epoxy or amine-containing intercalators or double-bond monomers) enable it to participate in the reaction with polymer macromolecules or polymerize, resultantly giving rise to an intercalated or exfoliated structure. In the solution casting of nanoclay-filled polymers, the selection of appropriate intercalators with intensive interaction with the solvent molecule is theoretically favourable for ultrasonication-assisted exfoliation before solution blending. Actually, the solvent entered the lamellar spacing and exfoliated the lamellar structure to single/few sheets, resulting in the formation of a homogeneous solution with the Tyndall effect or gel network.

In this chapter, following the target of progressively enhancing the fireretardant efficiency, the state of the art of LDH, halloysite and other nanoclays in fire-retardant applications are kept track of with the emphasis on revealing the multi-scale structure–performance link.

#### 4.2.2 Fundamentals

#### 4.2.2.1 Composition and Structure of Nanoclay and Derivatives

This chapter focuses on LDH, hallovsite and other species (e.g., sepiolite). Typical LDH is composed of positively charged metal hydroxide  $(M^{2+}/M^{3+})$ (OH)<sub>6</sub>) nanosheets pillared by negatively charged organic molecules in the gallery with the basic structural formula  $[M_{1-x}^{2+}M_x^{3+}(OH^{-})_2]^{x+}A_{x/n}^{n-}\cdot yH_2O$ . Herein,  $M^{2+}$  and  $M^{3+}$  represent divalent ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  or  $Fe^{2+}$ ) and trivalent ( $Al^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$  or  $Ni^{3+}$ ) metal ions. A and  $n^{-}$  are the intercalating anion and the valence, respectively. Notably, the x value reflecting the molar relation of the  $M^{2+}$  and  $M^{3+}$  range falls between 0.1 and 0.5. Actually, an *x* value less than 0.2 or more than 0.33 fails to generate the pure phase, which indicates the tendency to form Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub> phases.<sup>91</sup> The intercalated anions (e.g.,  $SO_4^-$ ,  $SO_3^-$ ,  $Cl^-$ ,  $COO^-$  and  $NO_3^-$ ) influence the gallery spacing, depending on the interaction between anions and charged lamellas, the size and the alignment pattern of anions. The ordered assembly of the basic constituents into LDH is categorized into co-precipitation, ion-exchange and regeneration. Visibly, the selection of different metal species and intercalating anions plays a critical role in catalytic and dispersion states, ultimately resulting in different combustion behaviours of polymer composites.

The kaolinite-like two-dimensional aluminosilicate layered structures with the formula  $Al_2Si_2O_5(OH)_4 \cdot nH_2O$  consist of an alumina octahedron and a silica tetrahedron in a 1:1 stoichiometric ratio.<sup>92,93</sup> Halloysite is formed when the layered structures are rolled into hollow nanotubular morphology towards a lower surface tension. On the basis of a hollow structure with a layered structure, the functional intercalation of a layered structure, hostguest incorporation of functional components or hierarchical assembly by functional nanoarchitecture are the prevailing strategies for the reinforced fire-retardancy application. The intercalation modification is demanded in normal cases in consideration of the compatibility with the polar or nonpolar polymer matrix for better dispersion. Different from two-dimensional nanosheets, one-dimensional nanotube tends to be dispersed in polymeric materials. Definitely, the structural parameters (*e.g.*, outer and inner diameter and length), particularly pore features, plays a critical role in fire retardancy.

## 4.2.2.2 Fire-retardant Mode of Action and Mechanism

The suppression of heat release is desirable to occur at the developing stage before and after ignition. Overheating at the developed flaming zone seriously surpasses the vapor- and condensed-phase flame-killing capacity. The fire-retardant mode of action of nanoclay-filled polymer composites is in major terms associated with the formation of a barrier effect to suppress the transfer of heat, oxygen and volatiles between the vapor phase and the condensed phase. In the LDH-filled composites, the catalysing effect towards the charring species or the intensive barrier effect during the melting/ pyrolysis state constitutes the dominant fire-retardant mechanism. The moisture release from LDH at a relatively low loading in nanocomposites after being heated to above 150 °C is not capable to reduce the efficient heat of combustion (EHC).<sup>94</sup> In terms of LDH-filled thermoplastic polymers, the direct incorporation of LDH preferentially suppresses the heat release in cone calorimetry in the "labyrinth" effect rather than flame spreading in the UL-94 test. The organic intercalation modification of LDH favours the nanodispersion towards better fire retardancy. In contrast, LDH-filled thermosetting, particularly epoxy, presents different combustion behaviours due to the strong charring capacity of epoxy. The addition of LDH imparts epoxy with an intumescent charring behaviour. The organically modified LDH particularly by sulfonate intercalators optimized the intumescent process of epoxy due to the positive effect of not only a higher exfoliation of LDH nanosheets but also sulfonate groups. The *in situ* decorated nanoscale catalysts or charring agent generates the interface-catalysis effect, optimizing the intumescent charring structure and promoting the fire retardancy. One exception emerges that the hierarchical and heterogeneous construction with LDH as the secondary block seemingly ruins the nanodispersion of LDH and deteriorates the fire retardancy in epoxy. However, the in situ incorporation of LDH on other heterogeneous substrates promotes the fire retardancy presumably on the basis of the catalysis of LDH.

The direct addition of halloysite (HNT) into thermoplastic polymers (*i.e.*, polypropylene) promotes the fire retardancy actually less remarkably than that of LDH due to a weaker "labyrinth" effect. The poorer fire retardancy is closely related to the "labyrinth" effect, which depends on the viscoelasticity response of polymer melt subjected to heat. Kashiwagi's and Tang's group detail the viscoelasticity response at different temperatures using a rheometer.<sup>95,96</sup> The integral effect of specific area, shape and surface

characteristics of nanofillers governs the viscoelasticity response of polymer composites. Intriguingly, the pyrolyzed volatile is proposed to flow into a HNT internal lumen and be released out slowly during thermal decomposition, which suppresses heat and smoke production. The suppressed volatile release infers higher thermal stability in the case of the non-active HNT surface. Anyhow, the direct addition of halloysite into thermosetting polymers (*e.g.*, epoxy) is not capable to increase and even ruin the fire retardancy attributed to the deteriorated char structure. The *in situ* decoration of a nanocatalyst or an organic fire retardant on the HNT surface or internal lumen consistently promotes the charring behaviour and accordingly fire retardancy. The surface-decorated nanocatalyst is associated with surfacecatalysis charring behaviour. In parallel, the nanocatalyst in the internal catalyst catalyses the absorbed volatiles for a better charring out of the lumen.

## 4.2.3 Layered Double Hydroxide

LDH is an excellent substitution for magnesium dihydroxide (MDH) and aluminum trihydroxide (ATH). The released moisture to cool down the flaming zone and the "labyrinth" effect of LDH in polymers are the dominant modes of fire-retardant action. The correlation between the "labyrinth" effect and the char microstructure is key to enhancing the fire-retardant efficiency of LDH assuming that the dispersion state remains the same.

## 4.2.3.1 Intercalated LDH as the Mono-component Fire Retardant

In both thermoplastic and thermosetting polymers, nanoscale dispersion is the regulating parameter. The intercalation of LDH with organic and inorganic anions for one aspect enlarges the gallery spacing for better dispersion and for another aspect incorporates the functional fire-retardant structure, e.g., catalytic agent or acidic agent. Wilkie et al.97 intercalated linear alkyl carboxylates ( $CH_3(CH_2)_nCOO^-$ , n = 8, 10, 12, 14, 16, and 20) into MgAl-LDH *via* an anionic exchange approach with the gallery spacing from 0.9 nm of the nitrate intercalator to 3.4 nm of the  $CH_3(CH_2)_{18}COO^-$  intercalator. The fire-retardant evaluation of LDH and an MMT-based nanofiller showed divergent trends, which illustrated that the dispersion state of LDH nanosheets was not as crucial as MMT nanosheets in determining fire retardancy. Zammarano et al.<sup>98</sup> observed the self-extinguishment of epoxy in a horizontal burning test with the organically-modified LDH for the first time among polymer nanocomposites. Phosphorus-containing anionic intercalator, e.g., ammonia polyphosphate (APP),<sup>99</sup> phosphorylated lignin<sup>85</sup> and other designed phosphorylated molecules in the LDH gallery not only contributed to the bigger gallery spacing but also participated in the surface charring behaviour towards a better fire retardancy of the polymeric nanocomposite. The comparison of intercalator size and LDH gallery spacing

illustrated that the complicated intercalators possessed various configurations depending on the rigidity, location of anions and interactions between intercalators. Amongst, Wang's research group conducted a series of work associated with the bio-based intercalator of LDH. LDH intercalated with carbon–carbon double bond-containing sulfonate β-cyclodextrin (DB-CD-BS) displayed a three-fold increase in the gallery spacing to 2.35 nm with the flower-like appearance relative to nitrate LDH.<sup>100</sup> The co-intercalation of sulfonate  $\beta$ -cyclodextrin, dodecylbenzenesulfonate (DBS) and taurine into LDH imparted epoxy with UL-94 V-0 rating at 6 wt% loading.<sup>101</sup> Furthermore, Wang *et al.*<sup>102</sup> co-intercalated a chalcone/s-CD host-guest structure (fCD), phytic acid (Ph) and DBS into the LDH gallery via one-step co-precipitation to prepare fLDH. Epoxy composites with 7 wt% fLDH presented a UL-94 V-0 rating and reduced pHRR by 66% with significantly enhanced UV resistance. In parallel, a ferrocene molecule was inserted into the hydrophobic cavity of sCD, which was intercalated into the LDH gallery in advance. The asprepared LDH-CD@Ferr imparted the epoxy matrix with UL-94 V-1 rating and 37% reduction of total smoke production (TSP) at 6 wt% loading in comparison with LDH-CD.<sup>103</sup> The investigation of the fire-safe mechanism illustrated that part of ferrocene entered the condensed phase to catalyse the charring reaction and the rest of ferrocene was released to the vapor phase for suppressing smoke. Other bio-based components, e.g., carrageenan, cardanol, eugenol and calix arenes, enabled to be used to prepare LDH intercalators for fire retardancy. The incorporation of catalytic metalcontaining anionic intercalators represents another direction to strengthen fire retardancy. The transition metal-containing  $[PW_{12}O_4]^{3-}$ ,  $[PMO_{12}O_4]^{3-}$  and  $MoO_4^{2-}$  were successfully incorporated into the LDH gallery for intumescent fire-retardant polymers.<sup>104,105</sup>

Additionally, the solution-processing method was employed to acquire the exfoliated LDH structure in a much higher loading than 5 wt%. Qu et al.<sup>106</sup> used the solution processing technique to fully exfoliate the dodecyl sulfate intercalated MgAl-LDH into PE-g-MAH with MgAl-LDH loading higher than 50 wt% for exceptionally enhanced thermal stability. More generally, the aprotic solvent formic acid (FA) acted as the prominent swelling agent of  $NO_3^-$  and  $ClO_4^-$  intercalated LDH.<sup>107</sup> Furthermore, the water-swelling LDH intercalators were discovered including lactate, acetate and propionate. On the basis of it, a new yet efficient approach called aqueous miscible organic solvent treatment (AMOST) emerged associated with the transformation of LDH from hydrophilic to hydrophobic to promote the dispersion of LDH in non-polar polymers. O'Hare's group reported two types of LDHs  $[Zn_2Al(OH_6)][B_4O_5(OH)_4]_{0.5}(Zn_2Al-borate)$  and  $[Mg_3Al(OH)_8][B_4O_5(OH)_4]_{0.5}$ (Mg<sub>3</sub>Al-borate) were completely exfoliated in the PP matrix even at 30 wt% loading with an acetone aqueous miscible solvent.<sup>108</sup> However, different from the LDH gel-derived nanocomposite, AMOST was hard to drive LDH exfoliation merely through xylene dispersion. Herein, the fully exfoliated state of LDH in polymers evidenced by X-ray diffraction pattern (XRD) was not sufficient.

The alternation of metal ions in LDH lamellas adjusts the catalytic capacity of lamellas as well as the gallery spacing. Zhao *et al.*<sup>109</sup> assembled  $SO_4^{2-}$  intercalated NiTi-LDH with a high specific surface area of 194.4 m<sup>2</sup> g<sup>-1</sup> and an averaged thickness of 1.93 nm. The only addition of 1 phr NiTi-LDH imparted silicon foam (SiF) with UL-94 V-0 rating and significantly suppressed smoke release. The insightful fire-safe mechanism was proposed associated with the catalytic charring towards the formation of a stable and compact char microstructure. The other utilization of LDH in fire retardancy was involved in the protective effect as the layer-by-layer (LBL) or direct coating construction block.<sup>110</sup>

### 4.2.3.2 Hierarchical Structure with LDH Blocks

Theoretically, the LDH block in the hierarchical structure is in the form of either a host component or a decorating guest component. Silica was preferentially assembled on DBS intercalated LDH (LDH-DBS) via the static electric interaction induced sol-gel process to prepare LDH-DBS@silica-1.3 wt% LDH-DBS(a) silica-1 endowed epoxy with self-extinguishment in the vertical burning mode with 3 wt% LDH-DBS.<sup>111</sup> Moreover, the ultrafine Ni(OH)<sub>2</sub> nanocatalyst was *in situ* grown on LDH-DBS *via* curricular coordination-induced growth to obtain LDH-DBS@Ni(OH)<sub>2</sub>. LDH-DBS@Ni(OH)<sub>2</sub> displayed a better dispersion in the epoxy matrix compared with LDH-DBS (see Figure 4.8a). A mere 3 wt% LDH-DBS@Ni(OH)<sub>2</sub> endowed epoxy with UL-94 V-0 rating. The mechanism investigation *via* dynamic charring analysis in multi-scales demonstrated that the interfacial-charring catalysis reinforced the intumescent structure towards more uniform and smaller open-pore chars (see Figure 4.8b).<sup>94</sup> The key governing factor in determining the hierarchical structure is the interaction between the LDH substrate and the decorating nanocomponent. The static electric-induced assembly process was the most commonly used. The other decorating catalysts, *e.g.*, ZIF-67,<sup>112</sup> were coated on the LDH surface to improve the fire-retardant efficiency. The basic fire-retardant mechanism was associated with either participation in or catalysis of the charring reaction of epoxy by the interface-located decorating component towards an optimized intumescence.

In parallel, the guest LDH blocks in the host substrates illustrated improved fire retardancy relative to the isolated LDH components and host substrates, which was remarkably contradictory with the requirement of a better dispersion. In a normal case, the simple blending of host substrates and guest LDH blocks presented the synergistic effect. Deeper integration of guest LDH blocks and host substrates actually facilitated the fire-suppression effect of the host substrate even though some fire-retardant performance loss was observed due to LDH blocks. Generally, LDH blocks possessing the catalysing capacity favoured the fire-retardant effect of the host substrate *via* the interfacial charring mode of action. Hierarchical hybrids with LDH blocks on various substrates, *e.g.*,  $g-C_3N_4$ ,<sup>113</sup> Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> whisker,<sup>114</sup> Mxenes,<sup>115</sup> rGO and CNTs, were reported for fire-retardant

polymers. In parallel, the *in situ* assembled LDH with intensive catalytic capacity on a conventional intumescent APP surface through the static electric effect or covalent linking was evidenced to be efficient in improving the fire-retardant efficiency.<sup>116</sup> Interestingly, Pan *et al.*<sup>117</sup> reported on NiCo-LDH *in situ* grown on LDH-DBS *via* the self-sacrificing etching of ZIF-67 to NiCo-LDH.

Until now, some kinds of hierarchical structures with LDH in the form of shells were fabricated as the fire-retardant reinforcer in polymers. Pan *et al.*<sup>118</sup> used the self-sacrificing approach to prepare the hierarchical structure with hydroxyl zinc stannate (ZHS) and NiCo-LDH (NCH) as the yolk and shell, respectively in order to promote the dispersion of ZHS nano-particles. An epoxy composite with 6 wt% targeted ZHS@NCH passed UL-94 vertical burning V-0 rating. Regretfully, the fire-retardant mode of action and the insightful mechanism were not clear. The relationship between micro-structure design and fire retardancy was not established to guide the future work.

## 4.2.3.3 LDH as the Synergist

As typical 2D lamellas, LDH and its nanohybrid are used as synergists based on the barrier effect or catalytic effect. LDH was proven to be effective as a synergist in intumescent, aluminum phosphinate (ALP)-based, metal hydroxidebased and nanofiller-based polymer system. Wang *et al.*<sup>119</sup> evidenced the superiority of ternary LDH over binary LDH in the cone calorimeter test (CCT) due to the incorporation of catalytic metal elements in the LDH lamellas. As a result, the microstructure of intumescent chars including pore size and pore size distribution was optimized attributed to the optimization of the crosslinking reaction. Gu *et al.* investigated the fire-retardant synergy between NiFe-LDH and AlP in polyurethane thermoplastic elastomer (TPU). Compared to UL-94 V-1 rating with the isolated addition of NiFe-LDH and AlP, the mixture of 6 wt% AlP and 1 wt% NiFe-LDH gave rise to UL-94 V-0 rating in TPU.<sup>120</sup>

## 4.2.4 Halloysite

The direct incorporation of HNT into thermoplastic and thermosetting charring polymers generated divergent fire retardancy results. In terms of the other fire-retardant applications, Grunlan *et al.*<sup>121</sup> used HNT as the coating component for suppressing the flammability of polyurethane foam (PUF).

#### 4.2.4.1 Grafting by Fire-retardant Molecules

The abundance of hydroxyls (Si-OH outer surface) provides the platform for surface chemistry. Marney *et al.*<sup>122</sup> electively grafted phenyl phosphonic acid (PPA) on the inner surface (Al-OH), leading to the reduced peak heat release rate by 55.3% in polyamide 6 (PA6) at a loading of 10 wt%. He *et al.*<sup>123</sup>

#### Mineral-derived Fire Retardants

repared P, N-decorated HNT (MA-PPA@HNT) *via* phenphosphinic acid intercalation and melamine adsorption. 2 wt% MA-PPA@HNT imparted PA6/AlPi (aluminum diethylphosphinate) with UL-94 V-0 rating relative to V-2 rating of PA6/AlPi/HNT. Yu *et al.*<sup>124</sup> grafted HNT outer surface with amine-polyhedral oligomeric silsesquioxane (NH<sub>2</sub>-POSS) with epoxy-bearing silane as the bridge. The as-obtained HNT-POSS at a 2 wt% loading endowed TPU with reduced pHRR by 60.0%. The condensed-phase fire-retardant mechanism was investigated, which involved the continuous and compact carbonaceous structure *via* HNT and the ceramified silicon network. Actually, the surface grafting of charring molecules on HNT promoted the charring behaviour of interfacial polymers, immobilizing HNT and stabilizing the microstructure of chars.

## 4.2.4.2 Hierarchical Structure with a Halloysite Block

The multi-layered structure of HNT (*i.e.*, inner cavity, in-between lumen, outer surface and the entity) enables to offer space for the hierarchical structural construction with HNT blocks. Wang *et al.*<sup>125</sup> successively modified HNT with polydopamine (PDA) and ultrafine Fe(OH)<sub>3</sub> nanodots to fabricate HNT@PDA@Fe(OH)<sub>3</sub> (see Figure 4.9a). 5 wt% HNT@PDA@Fe(OH)<sub>3</sub> endowed epoxy with an LOI value of 33.9% and a UL-94 vertical burning rating of V-1 (see Figure 4.9b). The ultrafine Fe(OH)<sub>3</sub> nanocatalyst primarily performed on PDA and epoxy molecules at a relatively low temperature with the formation of the char adhesives. Therefore, the fire chars of epoxy composites would be connected to the entity with a stronger barrier effect against heat and oxygen (see Figure 4.9c). The ultrafine size of the Fe(OH)<sub>3</sub> nanocatalyst and the PDA substrate with an intensive and fast charring capacity served as the key factors to govern the interfacial catalyst of the epoxy composite.

Dai *et al.*<sup>126</sup> fabricated two types of ultrafine copper-anchoring polyphosphazene modified HNT, i.e., HNT@PZF-Cu (hydroxyl) and HNT@PNF-Cu (amino) for fire-retardant epoxy. Relative to HNT@PNF-Cu, 3 wt% HNT@PZF-Cu reduced the pHRR, peak smoke production rate (pSPR) and carbon monoxide production by 52.2%, 40.3% and 64.2%, correspondingly. The mechanism investigation demonstrated that the Cu nanocatalyst promoted the thermal rearrangement and dehydrogenation of polyphosphazene for the interfacial charring reaction. In terms of effluent evolution, DFT analysis revealed the catalytic oxidation of CO and NO toxic gas via a series of intermediates. In parallel, Dai's research group<sup>127</sup> prepared the hierarchical "dots-core-shell" Ag@HNT@PZE with in situ anchored Ag in the inner cavity of HNT and a cross-linked polyphosphazene (PZE) on the outer surface of HNT. DFT calculations illustrated that CO was adsorbed on the Ag surface to form an intermediate peroxide OOCO complex with an energy barrier of only 1.15 kcal mol<sup>-1</sup>. Actually, the results verified the penetration behaviour of toxic CO into the HNT cavity which is then released.





## 4.2.4.3 Halloysite as a Host of Fire Retardants

The hollow tubular structure (~0.53 cm<sup>-3</sup> g<sup>-1</sup>) of HNT provides space for liquid highly efficient fire retardants (*e.g.*, BDP, DMMP and TPP). The theoretical DMMP addition is calculated as 60% at the highest level. The advantage of using the HNT-derived host-guest structure is avoiding the deterioration of mechanical properties due to the plasticizing effect and leaching effect of small-molecule liquid fire retardants. Takahara *et al.*<sup>128</sup> innovatively inserted hydrophobic BDP into the HNT lumen *via* the hydrophobic modification of HNT lumen by octadecyl phosphonic acid (ODP). The loading percentage was tested to be less than 10 wt%.

Ni *et al.*<sup>129</sup> adopted the vacuum-suction approach to loading organophosphorous DMMP into HNT to obtain the host-guest HNT-D with a DMMP percentage of 24.2 wt%. Interestingly, Wang *et al.*<sup>130</sup> reported the simultaneous grafting of the DOPO structure on the HNT inner and outer surface *via* maleic anhydride (MAH) mediating and infusing the DOPO derivatives into the HNT cavity to prepare HNT@MAH@DOPO (see Figure 4.10a).



**Figure 4.10** (a) Preparation of HNT@MAH@DOPO, (b) DTG curves of HNT and HNT derivatives, and (c) slow-release behaviour of HNT@MAH@DOPO.<sup>130</sup> Reproduced from ref. 130 with permission from Elsevier, Copyright 2017.

The total loading of the DOPO derivative was 16.0 wt%. PLA with 5 wt% HNT@MAH@DOPO displayed an LOI value of 38.0% and reached UL-94 V-0 compared with the simple mixture (LOI = 30.8% and UL-94 V-0). The work linked the dominant slow-release behaviour of DOPO derivatives and improved fire retardancy, which resulted in the highly efficient utilization of phosphorus-containing radicals. Also, the slow-release behaviour of P-containing species was proposed to connect with different locations of P elements on HNT (see Figure 4.10b and c). Sun et al.<sup>131</sup> filled polysiloxane into HNTs (HNTs-Si) as the synergistic agent of intumescent PP. The pHRR and pSPR of intumescent PP with HNTs-Si dropped by 31% and 26% separately relative to that containing HNTs. Anyhow, the limited cavity volume in single HNT poses to be a serious barrier to incorporating a higher loading of guest molecules. Lvov et al.<sup>132</sup> reported the enlargement of the HNT cavity via the selective etching of inner alumina with condensed sulfuric acid. The lumen diameter was increased from 15 nm to 25 nm with a 2-3 increase in capacity.

In addition to the above-reviewed three modification approaches of HNT for fire retardancy, the use of virgin HNT as the synergist of the intumescent or diethyl phosphinate (ALP)-based system was verified.<sup>133</sup> It was proposed that the tubular HNT acted as the bridge to connect different char pieces to the compact and continuous entity. The active acidic catalytic sites of Si–OH presumably presented certain catalytic charring capacities.

## 4.2.5 Other Nanoclays as Fire Retardants

Other nanoscale clays, e.g., sepiolite,<sup>134</sup> palygorskite<sup>135</sup> and talc,<sup>136</sup> presented notable fire retardancy towards polymers. However, the fireretardancy efficiency is not satisfactory due to the intrinsic fire-retardant features of weak dehydration towards cooling the vapor phase and the poor barrier effect. As a fiber-like clay, sepiolite was applied as host blocks to form the phosphorus-containing organic-inorganic hybrid, to form the hierarchical nanohybrid or as the synergistic agent in intumescent fire-retardant systems. Zhang et al.<sup>137</sup> reported using amino silane to graft the DOPO structure to prepare a hybrid SEP-DOPO with a grafting ratio of 12.8%. Tripathi et al.<sup>137</sup> adopted polydopamine (PDA) and phosphorous acid to successively modify the sepiolite to fabricate Spl-PDA-EDA-P. 5 wt% Spl-PDA-EDA-P imparted PP with an LOI value of 30.2%, accompanied by a notable enhancement of melt flow, 70% maintaining of tensile strength. In parallel, Hu et al.<sup>138</sup> in situ decorated NiFe-LDH on sepiolite to obtain a-SEP@LDH via acid treatment and a co-precipitation method. Epoxy composites with 2.3 wt% a-SEP@LDH reached a V-1 rating in the UL-94 test and possessed an LOI value of 31.1%, accompanied by a 21% reduction of pHRR. The basic fire-retardant mode of action was associated with interface catalysis towards a stronger charring behaviour for the compact and continuous epoxy char microstructure.

#### 4.2.6 Conclusion and Perspective

As an environmentally benign and green fire retardant, nanoscale clays enjoy a massive focus in the academic and industrial community. This chapter discusses the state of the art of dominantly layered double hydroxide, halloysite and sepiolite and comparatively analyzed their fire-retardant mechanism and mode of action. The key governing factors of how the design of the hybrid structure and hierarchical microstructure influences the charring behaviour and structure should be clarified. The importance of interface issues is widely recognised in constructing high-quality chars. In the future, more effective strategies and designs to strengthen interfacial fire retardancy are desirable. The multifunctionality of nanoscale clays and solutions to industrial applications, *e.g.*, thermal stability and processing ability, are also focused on.

## 4.3 Other Mineral-derived Fire Retardants

#### 4.3.1 Fly Ash

FA is a by-product of thermal power plants, and its annual output reaches approximately 500 million tons, bringing great pollution to the ecological environment.<sup>139–141</sup> However, only a handful of fly ash is recycled in the construction industry, mainly in cement and concrete manufacturing, while the remainder is disposed of in landfill sites.<sup>142</sup> Hence, the reutilization of fly ash is significant yet challenging and has received tremendous attention.

FA is a relatively fine powder, and its particle diameter is mainly between 0.1 and 400  $\mu$ m.<sup>143</sup> FA consists of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), calcium oxide (CaO) and a small number of other oxides (see Table 4.1). FA is classified as hazardous waste in the European Waste Catalog because it contains high levels of soluble salts and heavy metals, *e.g.*, lead, cadmium

| Component                      | Unit                  | Content |
|--------------------------------|-----------------------|---------|
| SiO <sub>2</sub>               | wt%                   | 67.89   |
| $Al_2O_3$                      | wt%                   | 21.92   |
| Fe <sub>2</sub> O <sub>3</sub> | wt%                   | 3.94    |
| K <sub>2</sub> O               | wt%                   | 1.36    |
| NaOH                           | wt%                   | 1.30    |
| TiO <sub>2</sub>               | wt%                   | 1.28    |
| MgO                            | wt%                   | 0.63    |
| CaO                            | wt%                   | 0.57    |
| SO <sub>3</sub>                | wt%                   | 0.42    |
| Na <sub>2</sub> O              | wt%                   | 0.36    |
| MnO                            | wt%                   | 0.03    |
| pН                             |                       | 7.4     |
| Density                        | $g  \mathrm{cm}^{-3}$ | 2.21    |

**Table 4.1** Chemical characterization of common FA.

and zinc.<sup>144</sup> Hence, great efforts have been devoted to the exploration of FA applications. In recent years, some researches have reported that FA can be used as a mineral-derived flame retardant to enhance the fire safety of polymeric materials due to its chemical composition, high thermal stability and low price.

Soyama *et al.* reported that a polycarbonate with 25 wt% FA can achieve a UL-94 V-0 classification.<sup>145</sup> The enhanced flame retardancy was mainly due to the hydrogen bond between the hydroxy group on the FA surface and the carbonate group of the polycarbonate. During burning, this bond not only thermally stabilizes the polycarbonate, but also isomerizes the polycarbonate, thus promoting char formation. However, the addition of 25 wt% FA significantly compromised the toughness of the polycarbonate, as reflected by a 90.7% decrease in impact strength. Meanwhile, Mahadeva et al. fabricated flame-retardant and smoke-suppressive epoxy composites by adding FA.<sup>146</sup> The addition of 20% FA brought about 33.9%, 17.0% and 28.6% reductions in the peak heat release rate, total heat release and total smoke release of the epoxy composite. Besides polycarbonate and epoxy resin (EP), FA has also been applied in the fabrication of flame-retardant polyurethane (PU), silicone rubber (SR) and poly(vinyl chloride) (PVC).<sup>140,144,147</sup> Hence. these works have demonstrated that FA can be used as a flame retardant for polymeric materials, but it needs a high loading level to achieve satisfactory flame retardancy.

Similar to other mineral-derived flame retardants, FA also tends to agglomerate within the polymer, and thus some chemicals have been applied to modify FA to enhance its dispersion in the matrix. For instance, Nguyen recently reported a stearic acid-decorated FA, which increased the limiting oxygen index (LOI) of the epoxy composite to 23.2% and decreased the burning rate to 16.28 mm min<sup>-1</sup> when its content was 20 wt%.<sup>148</sup> Notably, under the same content, the stearic acid-decorated FA was more effective in maintaining the mechanical properties of the epoxy composite relative to the unmodified FA, demonstrating the importance of surface decoration. Additionally, Radzi *et al.* prepared a NaOH-treated FA, which was also more compatible with the polymer matrix than the untreated FA.<sup>149</sup>

FA has also been combined with other flame retardants to form flame retardant polymeric composites. Nguyen and Nguyen applied FA and multiwalled carbon nanotubes (MWCNTs) to improve the fire retardant and mechanical properties of epoxy resin.<sup>150</sup> Their results showed that the limiting oxygen index of the epoxy composite (FAST5) with 0.04 wt% MWCNTs and 40 wt% fly ash increased from 20.6% of the unmodified EP to 26.8%. Moreover, the tensile, compressive and impact strengths of FAST5 were increased by 5.2%, 44.2% and 126.3% relative to pure EP. Hence, the combination of FA and MWCNTs can endow EP with enhanced flame retardancy and mechanical properties. Additionally, Zhou *et al.* combined FA with intumescent flame retardant (IFR), composed of ammonium polyphosphate (APP) and pentaerythritol (PER), for the fabrication of flame retardant thermoplastic polyurethane (TPU).<sup>151</sup> As presented in Figure 4.11, the TPU with 15 wt% IFR and 10 wt% FA exhibited a lower peak heat release rate,



**Figure 4.11** Heat release rate (a), total heat release (b), smoke production rate (c) and total smoke production (d) curves of TPU and TPU/IFR/FA composites.<sup>151</sup> Reproduced from ref. 151 with permission from John Wiley & Sons, Copyright © 2019 John Wiley & Sons, Ltd.

total heat release, peak smoke production rate and total smoke production than those of the TPU with 25 wt% IFR, demonstrating better flame retardancy and smoke suppression due to the synergistic effect between IFR and FA. During combustion, IFR and FA jointly functioned in the condensed phase to promote the TPU matrix to form an intumescent and dense char, which suppressed heat transfer and volatile diffusion.

## 4.3.2 Sodium Silicate (Na<sub>2</sub>SiO<sub>3</sub>)

Sodium silicate (SS), also named sodium metasilicate or water glass, is one kind of soluble silicate, which includes approximately 21-34 wt% SiO<sub>2</sub> and 6-18 wt% Na<sub>2</sub>O.<sup>152</sup> In recent years, SS has been extensively applied as a flame-retardant filler for various polymeric materials.<sup>153</sup> As a mineral-derived flame retardant, sodium silicate will form a solid foamy char shield under heating, which suppresses the flame spread during burning.<sup>154</sup> However, SS absorbs large amounts of H<sub>2</sub>O when exposed to air, which will significantly restrict its effectiveness over time.

Tsuyumoto introduced amorphous sodium silicate (ASL) into poly(ethyleneco-vinyl acetate) (EVA) and investigated the impact of ASL on the flame retardancy of EVA.<sup>155</sup> As 33 wt% or more of ASL was added, the EVA composite exhibited self-extinguishing properties and passed the UL-94 V-0 classification. Under the same addition, the UL-94 rating of the EVA composite with ASL was much higher than that of the EVA composite with  $Mg(OH)_2$ , indicating that the flame-retardant efficiency of ASL was superior to that of  $Mg(OH)_2$ . The superior flame retardancy of ASL was mainly because it transformed into a glass shield, which covered sample surfaces to retard the exchange of heat and oxygen during burning.

Sahoo *et al.* prepared poly(butyl acrylate) (PBA)/sodium silicate (SS) nanocomposites using an emulsifier-free emulsion technique in the presence of a Cu( $\pi$ )/glycine chelate complex and ammonium persulfate.<sup>156</sup> PBA was intercalated into the SS layer, which endowed the PBA/SS nanocomposites with improved thermal stability. Moreover, the cone calorimeter results in Figure 4.12 presented that adding 5 wt% SS obviously reduced the heat release and smoke generation of PBA. However, SS improved the flame retardancy of PBA at the expense of mechanical properties. Cheng and Zhou also used sodium silicate to flame retardant polyurethane materials, and their results showed that 33.3% of SS can increase the LOI of polyurethane to 39.5% and reduce the peak heat release rate by 69.1%.<sup>157</sup> Similarly, the enhanced flame retardancy of the polyurethane composite was attributed to the promoting carbonization effect of SS. These works confirmed that SS can be employed as a flame retardant for different polymeric materials, but it needed a high loading level to achieve flame retardancy.

Similar to many mineral-derived flame retardants, sodium silicate is often used with other flame retardants for the fabrication of synergistic flame-retardant polymers. Susilo *et al.* prepared flame-retardant glass fiber reinforced unsaturated polyester resin (GF/UPRs/ATH/SS) composites by adding aluminum trihydroxide (ATH) and SS.<sup>158</sup> The burning tests of the GF/UPRs/ATH/SS composites were undertaken in accordance with ASTM D635, and the results showed that the time to ignition of the composite was increased and the burning rate was reduced with the introduction of ATH



**Figure 4.12** Heat release rate (a) and smoke production rate (b) plots of PBA and the PBA/5%SS nanocomposite.<sup>156</sup> Reproduced from ref. 156 with permission from Elsevier, Copyright 2008.

and SS. The composite with 20 wt% ATH and 10 wt% SS exhibited selfextinguishing properties because ATH absorbed heat to release water vapor and SS promoted the formation of glassy and continuous chars in the burning procedure.

Sun *et al.* introduced ammonium polyphosphate (APP), sodium silicate (SS) and sodium fluorosilicate (SFS) into poly(vinyl alcohol) (PVA) for the preparation of intumescent fire-retardant, self-healing, PVA-based (PVA/SSA) coatings, applied in plywood.<sup>159</sup> The obtained PVA/SSA coatings exhibited superior charring capacity, of which the char yield can reach up to 45.1% under a nitrogen atmosphere. The fire resistance of the coatings was studied using the 'Big panel method'. During the test, the plywood coated with pure PVA was cracked at about 114 s under flame, while the cracking time of plywood with PVA/SSA was significantly increased, which can finally be up to 200 s. The improved fire resistance of PVA/SSA coatings was mainly due to the formation of an inorganic silicate network by SS and SFS and the generation of intumescent chars by PVA and APP. Hence, SS can also be used as a synergistic flame retardant for commercial flame retardants, *e.g.*, ATH and APP, but its addition is still very high, which may restrict its practical applications in the industry.

#### 4.3.3 Kaolin

Kaolin is a two-layered hydrous alumina silicate with the general chemical formula  $Al_2Si_2O_5(OH)_4$  (see Figure 4.13), which is composed of chemically bonded layers of silica and gibbsite (hydrous alumina).<sup>160,161</sup> Kaolin is a cost-effective mineral material and is often applied in polymer composites.<sup>162–164</sup> In recent years, kaolin also serves as a flame retardant for different polymeric materials.

Zhang *et al.* used kaolin as a synergistic flame retardant to strengthen the flame-retardant performances of IFR, consisting of APP and PER.<sup>163</sup> Kaolin

(a) (b)

**Figure 4.13** The structure (a) and field emission scan electron microscopy image (b) of kaolin.<sup>160,162</sup> Adapted from ref. 160 with permission from the Royal Society of Chemistry. Adapted from ref. 162 with permission from Elsevier, Copyright 2018.

and IFR were introduced into polypropylene (PP), and their impacts on the flame retardancy were investigated. The PP composite with 40 phr IFR (PP/40 phr IFR) showed an LOI of 30.0% and a UL-94 V-0 rating, while replacing 2 phr IFR with kaolin kept the UL-94 rating of the PP/38 phr IFR/2 phr K composite at V-0 and increased the LOI to 33.0%. Meanwhile, the peak heat release rate and peak smoke production rate of the PP/38 phr IFR/2 phr K composite were 30.2% and 28.6% lower than those of the PP/40 phr IFR composite, respectively. The improved fire safety was attributed to the formation of more compact char layers *via* the synergistic effect of IFR and kaolin. In addition to IFR, Jang applied kaolin as a synergistic flame retardant of bisphenol A bis(diphenyl phosphate) (BDP) to flame retardant polycarbonate.<sup>165</sup> Their results showed that the combination of BDP and kaolin increased the UL-94 rating of polycarbonate to V-0 but decreased the robustness and toughness. The synergistic effect of kaolin and commercial flame retardants, magnesium hydroxide and Exolit® OP1311. was also investigated by different groups, and their results confirmed that the introduction of kaolin and commercial flame retardants increased the density and rigidity of the char foam, bringing about improved flame retardancy.<sup>166,167</sup> All these works demonstrate that the combination of kaolin and other flame retardants can improve the fire safety of polymeric materials.

The incorporation of kaolin often sacrifices the mechanical properties of polymers due to its strong tendency to self-agglomerate. The surface of kaolin is covered with silanol groups, which are capable of reacting with organics to prevent the agglomeration of kaolin within the polymer matrix and improve the flame retardancy. Tang *et al.* prepared an acid-activated kaolin (Acid-Kaol) *via* calcination and surface acid treatment and investigated its impact on the flame retardancy of IFR-containing polypropylene composites.<sup>168</sup> Under the same addition, the Acid-Kaol exhibited a better promoting char-formation effect than the unmodified kaolin. The IFR/Acid-Kaol-containing polypropylene composite showed superior flame retardancy to the IFR/kaolin-containing polypropylene composite due to its better carbonization capacity. In addition, their group also prepared an ammonium sulfamate (AS)-intercalated kaolin and further confirmed that the surface modification can strengthen the flame-retardant performance of kaolin.<sup>161</sup>

Swoboda *et al.* modified kaolin with triphenylphosphite (TPP) and investigated the impact of TPP-grafted kaolin on the mechanical and flame-retardant properties of recycled polyethylene terephthalate (PET).<sup>169</sup> The surface modification endowed kaolin with improved dispersion within the matrix, and thus the PET composite with TPP-grafted kaolin exhibited an LOI of 29.7%, with a 56.1% reduction in the peak heat release rate and a 64.3% increase in the bending modulus relative to virgin PET, demonstrating the improved flame retardancy and mechanical properties. Hence, the well-dispersed TPP-grafted kaolin can simultaneously enhance both flame retardancy and mechanical properties of PET.

Ou *et al.* prepared urea-modified kaolin (KU) and introduced KU, double pentaerythritol (DPER) and silicon dioxide (SiO<sub>2</sub>)-grafted APP (SiO<sub>2</sub>@MAPP)

into low density polyethylene (LDPE).<sup>170</sup> The LDPE with 16.7 wt% SiO<sub>2</sub>@MAPP and 8.3 wt% DPER showed an LOI of 24.1% and cannot pass the UL-94 test, while the LDPE with 1.4 wt% KU, 15.7 wt% SiO<sub>2</sub>@MAPP and 7.9 wt% DPER presented an LOI of 27.2% and a UL-94 V-1 rating. Such results demonstrated that replacing part of DPER and SiO<sub>2</sub>@MAPP with KU can improve the flame retardant properties. Meanwhile, the introduction of KU increased the thermal stability, tensile strength and elongation at break of LDPE. Thus, the urea-modified kaolin featured multiple functions towards LDPE.

Kaolin is often used as a synergistic flame retardant of commercial flame retardants for the fabrication of flame-retardant polymers. Additionally, surface modification can reduce the agglomeration of kaolin in the polymer matrix and endow kaolin with multiple functions.

## 4.3.4 Huntite and Hydromagnesite

Huntite and hydromagnesite (HH) comprise one kind of naturally occurring mixed carbonate minerals, and the chemical formula of huntite is  $Mg_3Ca(CO_3)_4$  and the chemical formula of hydromagnesite is  $Mg_5(CO_3)_4(OH)_2 \cdot 4(H_2O)$ . HH features non-corrosiveness, is halogen-free, prouces low smoke production, and exhibits low combustion and environmentally safe characteristics, and thus it has been applied as a flame retardant for various polymers since the late 1980s.<sup>171,172</sup> HH has a high initial degradation temperature (220–240 °C), and thus it can meet the processing requirements of different polymers.<sup>173</sup> HH decomposes endothermically to generate MgO, CaO, H<sub>2</sub>O and CO<sub>2</sub> (see Figure 4.14) at high temperatures, and thus it provides cooling and strengthens the char layers during burning.<sup>174</sup>

Touré *et al.* prepared flame-retardant ethylene–propylene composites by introducing HH, and investigated the impact of HH content on the mechanical and flame-retardant performances.<sup>175</sup> Their results showed that adding 41.8 wt% HH increased the LOI from 18.3% of the unmodified ethylene–propylene copolymer to 24.5%. Meanwhile, the introduction of HH increased the flexural modulus but reduced the Charpy impact. The enhanced flame retardancy was mainly due to two physical actions of HH: the endothermic process in the condensed phase and dilution in the gaseous phase. However, HH improved the flame retardancy of the ethylene–propylene copolymer at the expense of toughness.

Yurddaskal and Celik used HH to prepare flame-retardant polypropylene and investigated the impact of different HH contents on the properties of polypropylene.<sup>176</sup> Their results showed that the introduction of HH

Mg<sub>3</sub>Ca(CO<sub>3</sub>)<sub>4</sub> 
$$\xrightarrow{450-800 \ ^{\circ}C}$$
 3MgO + CaO + 4CO<sub>2</sub>  
Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4(H<sub>2</sub>O)  $\xrightarrow{220-550 \ ^{\circ}C}$  5MgO + 5H<sub>2</sub>O + 4CO<sub>2</sub>

Figure 4.14 The decomposition reactions of huntite and hydromagnesite under heating.

significantly increased the char yield and Young's modulus of PP, but obviously reduced the tensile strength. The decreased mechanical strength was mainly due to the poor interaction between HH and PP. The neat PP showed an LOI of 17.1% and cannot achieve any UL-94 rating. The introduction of 50 wt% HH increased the LOI and UL-94 rating of PP to 25.5% and V-0, respectively, because HH prolonged the ignition time of PP and impeded dripping.

Similar to other mineral-derived flame retardants, HH is often employed as a synergistic flame retardant of commercial flame retardants to fabricate flame-retardant polymeric materials. Guler *et al.* reported a flame-retardant TPU with HH and expandable graphite (EG).<sup>173</sup> The integration of HH and EG did not reduce the initial decomposition of TPU but significantly increased the carbonization. The LOI values of virgin TPU and the TPU composite with 50 wt% HH were 21.2% and 25.7%, and both of them cannot pass the UL-94 test. By contrast, the TPU composite with 25 wt% HH and EG jointly improved the flame retardancy of TPU, mainly by facilitating the formation of an intumescent and compact char to retard the burning of the matrix. However, the mechanical properties of TPU were gradually reduced with the increasing HH and EG contents. In addition, their group also used HH as a synergistic flame retardant TPU.<sup>177,178</sup>

Yurddaskal *et al.* introduced HH and antimony trioxide nanoparticles to prepare flame-retardant acrylonitrile–butadiene–styrene (ABS) composites.<sup>179</sup> Similarly, the addition of HH and antimony trioxide increased both the initial decomposition and char yield of the ABS composite. The ABS composite with 50 wt% HH or antimony trioxide can only achieve a UL-94 V-1 classification, while the composite with 40 wt% HH and 10 wt% antimony trioxide or 30 wt% HH and 20 wt% antimony trioxide can pass the UL-94 V-0 classification. However, both HH and antimony trioxide suffered from a negative effect on the mechanical properties of ABS, thus the tensile strengths of the obtained composites were obviously decreased.

In general, huntite and hydromagnesite can be used as a flame retardant for various polymers, but it suffers from a low flame-retardant efficiency. Hence, many scientists combined huntite and hydromagnesite with other flame retardants, and such a combination can achieve high flame retardancy, but the negative effect of huntite and hydromagnesite on the mechanical properties should be noted and addressed.

#### 4.3.5 Boehmite

Boehmite is an aluminum oxyhydroxide (AlOOH), and it is preferentially applied as a precursor to produce aluminum oxides.<sup>180,181</sup> Boehmite is composed of nanosheets of octahedral aluminum ions with surface hydroxyl groups. Similar to aluminum hydroxide, boehmite absorbs a lot of heat to release water vapor and generate thermally-stable alumina (Al<sub>2</sub>O<sub>3</sub>), and thus

it can also be used as a mineral-derived flame retardant for polymers.<sup>182</sup> As presented in Figure 4.15, the decomposition temperature of boehmite ( $\sim$ 350 °C) is higher than that of aluminum hydroxide ( $\sim$ 270 °C), which enables it to be processed at a higher temperature.<sup>183</sup>

Camino *et al.* fabricated a flame retardant ethylene-vinyl-acetate (EVA) composite by introducing 50 wt% boehmite.<sup>35</sup> The LOI of the obtained EVA composite was increased from 9% of virgin EVA to 24.5–25.0%, but it still cannot pass the UL-94 test. The increased LOI was mainly due to the replacement of flammable EVA with boehmite and the condensed-phase



**Figure 4.15** The scanning electron microscopy image (a) and thermogravimetric analysis curve under  $N_2$  (b) of boehmite.<sup>181,183</sup> Reproduced from ref. 181 with permission from John Wiley & Sons, Copyright © 2010 John Wiley & Sons, Ltd. Reproduced from ref. 183 with permission from Elsevier, Copyright 2013.

effect of boehmite. However, the mechanical properties of EVA were gradually reduced as the boehmite content increased.

Laachachi *et al.* investigated the impacts of boehmite on the thermal stability and flammability of poly(methyl methacrylate) (PMMA).<sup>184</sup> The initial degradation temperature and char yield of PMMA under air were gradually increased as the boehmite loading level increased (see Figure 4.16). With the introduction of boehmite, the time to ignition of PMMA was prolonged, and the peak heat release rate and total heat release were reduced (see Figure 4.16). For instance, adding 20 wt% boehmite increased the time to ignition by 13 s, and reduced the peak heat release rate and total heat release by 44.2% and 11.6%. The improved flame retardancy can be attributed to the replacement of PMMA with boehmite, the endothermic decomposition of boehmite, the dilution effect of water vapor from boehmite and the barrier and catalytic carbonization effects of boehmite and Al<sub>2</sub>O<sub>3</sub>. Besides EVA and PMMA, boehmite had also been applied for the fabrication of flame-retardant epoxy resin,<sup>185</sup> polylactide,<sup>186</sup> polyurethane,<sup>187</sup> poly(butylene succinate)<sup>188</sup> and polyethersulfone.<sup>183</sup>

Boehmite had also been used as a synergist of other flame retardants. Recently, Li studied the synergistic effect of melamine cyanurate (MCA) and boehmite on the flame retardancy of polyamide 6 (PA6).<sup>189</sup> PA6 exhibited an LOI of 22.8% and it cannot achieve any UL-94 rating. With the introduction of 11 wt% MCA and 4 wt% boehmite, the LOI and UL-94 rating of PA6 composite were increased to 33.8% and V-0, respectively. Compared with PA6, the PA6 composite with 11 wt% MCA and 4 wt% boehmite exhibited 60.0% and 40.6% reductions in the peak heat release rate and total heat release. Such results indicated that introducing appropriate amounts of MCA and boehmite into PA6 can achieve synergistic flame retardancy.

Lin *et al.* prepared an organic-inorganic flame retardant (BM@Al-BuPPi) by the reaction of isobutyl-phenylphosphinic acid (Bu-PPiA) and



**Figure 4.16** (a) The thermogravimetric analysis curves under air and (b) heat release rate plots of PMMA composites with different boehmite contents.<sup>184</sup> Reproduced from ref. 184 with permission from Elsevier, Copyright 2009.

boehmite and used it to flame retardant PA6.<sup>190</sup> With the addition of 15 wt% BM@Al-BuPPi, the PA6 composite exhibited an LOI of 35.0% and a UL-94 V-0 rating. Notably, BM@Al-BuPPi was more effective in maintaining the mechanical properties of PA6 than Bu-PPiA and boehmite. Thus, BM@Al-BuPPi can effectively enhance the flame retardancy of PA6 and maintain its mechanical properties. The enhanced flame retardancy of PA6 was because boehmite and Al-BuPPi jointly strengthened the char layer under fire, thus retarding the exchange of heat and oxygen.

These works have confirmed that boehmite can be applied in the fabrication of flame-retardant polymer composites, and the combination of boehmite and other common flame retardants is an effective way to achieve satisfactory flame retardancy. However, to realize the practical application of boehmite in the flame retardant field, its efficiency should be improved.

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