Layered double hydroxides as thermal stabilizers for Poly(vinyl chloride): A review

Yixuan Guo, Fabrice Leroux, Weiliang Tian, Dianqing Li, Pinggui Tang,
Yongjun Feng

Layered double hydroxides as thermal stabilizers for Poly(vinyl chloride): A review

Yixuan Guo[a], Fabrice Leroux[b], Weiliang Tian[c], Dianqing Li[a], Pinggui Tang[a], Yongjun Feng[a,c*]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, No. 15 Beisanhuan East Road,*

Beijing 100029, China

[b] *Université Clermont Auvergne, Institut de Chimie de Clermont-Ferrand ICCF, UMR-CNRS n 6296, F_63171 Aubière, France*

[c] *Key Laboratory of Chemical Engineering in South Xinjiang, College of Life Science, Tarim University, Alar 843300, P. R. China*
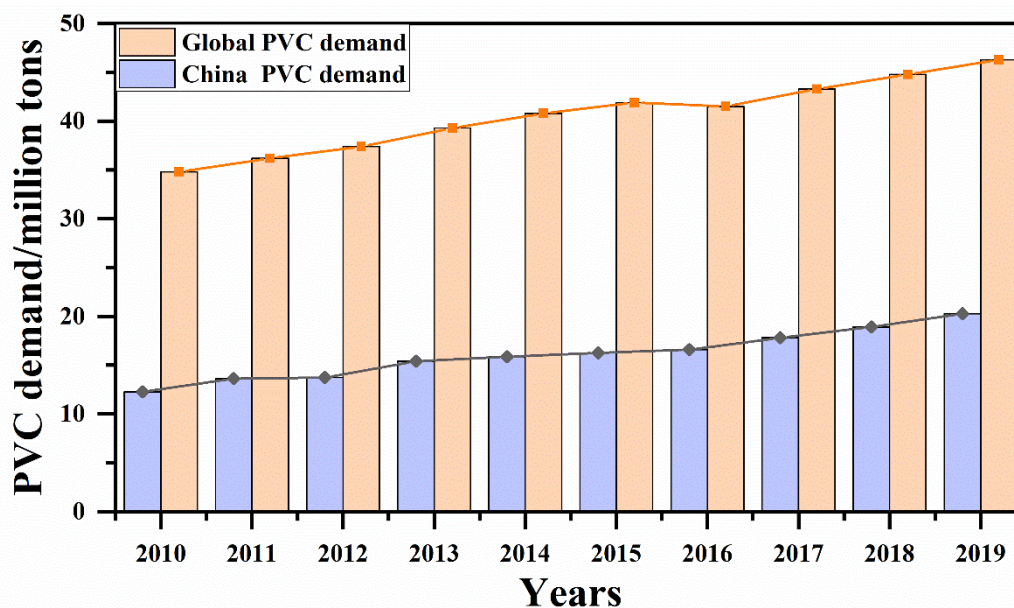
Abstract: Poly(vinyl chloride) (PVC), an important thermoplastic polymer widely-used in various fields, requires the use of thermal stabilizers to enhance its thermal stability during polymer processing and practical applications because of the poor thermal stability. Layered double hydroxides (LDHs), two-dimensional anionic layered and versatile filler, are widely considered to be one kind of high-efficient and environment-friendly PVC thermal stabilizers. Interestingly, it is expected to gradually replace the traditional toxic thermal stabilizers such as lead salts. The recent development of LDH thermal stabilizers in PVC resins is here reviewed from four relevant aspects: - the thermal stabilization mechanism provided by LDHs, - the chemical composition of metal layers and - of interlayer guests, and - the dispersion state of LDH in PVC composites. The review provides a current picture to help in the choice of manufacturing of high-performance LDH thermal stabilizers.

Key Words: Poly(vinyl chloride); Thermal stabilizer; Layered double hydroxides; Intercalation compounds; Filler dispersion state

1. Introduction

Poly(vinyl chloride) (PVC), produced by polymerization of vinyl chloride, is the most versatile thermoplastic polymer after polyethylene (PE) and polypropylene (PP) around the world. PVC resins have a wide variety of advantages, e.g., excellent flame retardancy, smoke suppression, low price, corrosion resistance, electrical insulating properties, high mechanical strength, and ease of processing. Owing to these excellent features, PVC products have been widely applied in chemicals, automobile, construction, food, packaging, aviation, electronic components, and other various
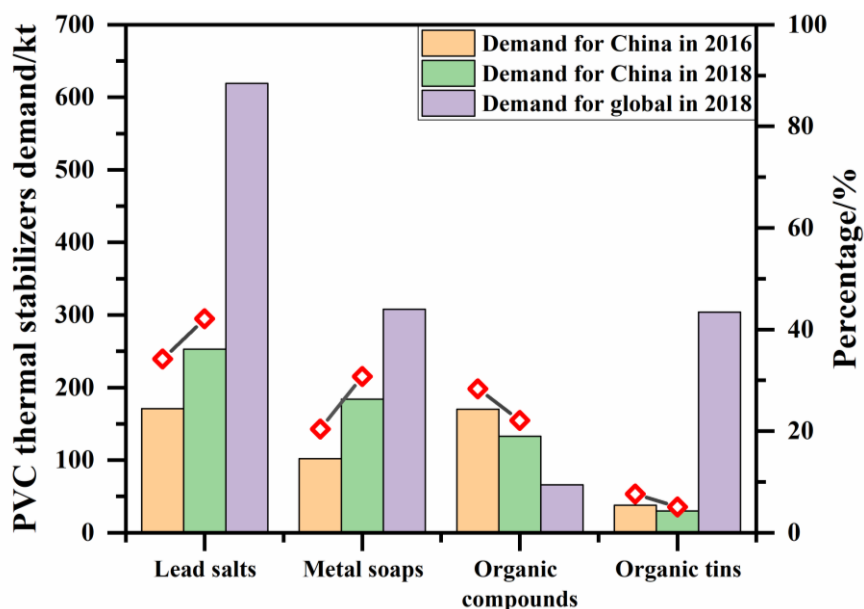
Corresponding author.

E-mail address: yjfeng@mail.buct.edu.cn (Y.J. Feng).

industries (Titow, 1990; Ma et al., 2019). According to market research institute IHS Markit (https://ihsmarkit.com/), overall global demands for PVC grew from 2010 to 2019 and reached 46.3 million tons in 2019 with a compound annual growth rate (CAGR) of 2.9 %. North-East Asia provides the biggest share of PVC consumers with 54 %, and China, the largest PVC consumer, alone has 20.3 million tons and keeps an annual growth of 5.1 % between 2010 and 2019 (Fig. 1). Also, the global PVC production is estimated to grow at a CAGR of 3.5 % from 2019 to 2023, determined by high demands and living standards.

Fig. 1 global and Chinese PVC demand and relative variation tends from 2010 to 2019.

However, PVC has poor thermal stability and is easy degraded to produce hydrogen chloride (HCl) gas during processing and its application due to the unstable structure (e.g., allyl chloride, tertiary chloride, and head-to-head structure) in its polymer chains. Simultaneously, the formation of carbon-carbon double bonds can active the adjacent carbon to further generate more double bonds as well as HCl. In turn, the HCl gas accelerates catalytically the degradation process of PVC, causing the formation of polyene sequences of π-conjugated double bonds. This process is called the zipper autocatalytic dehydrochlorination, which leads to the discoloration and deterioration of mechanical properties of PVC products as a function of time. Particularly, the thermoforming temperature (160-210 °C) of PVC products is much higher than their thermal degradation temperature (about 100 °C), which severely affects the processing and practical application of PVC products (Wypych et al., 2015). Therefore, it is necessary to use special thermal stabilizers to restrain thermal damage due to the high temperatures occurring during the polymer process (Fisch et al., 1999). Indeed, PVC thermal stabilization has been addressed since the early 70's when PVC was still the second

industrial polymer by production. Since then, a huge amount of literature has been published which led to the understanding of the basic mechanisms of PVC degradation and stabilization. One of the purposes of the review is to supply a state of the art, including the historical aspect which has a fundamental informative role in understanding the evolution to the present status.
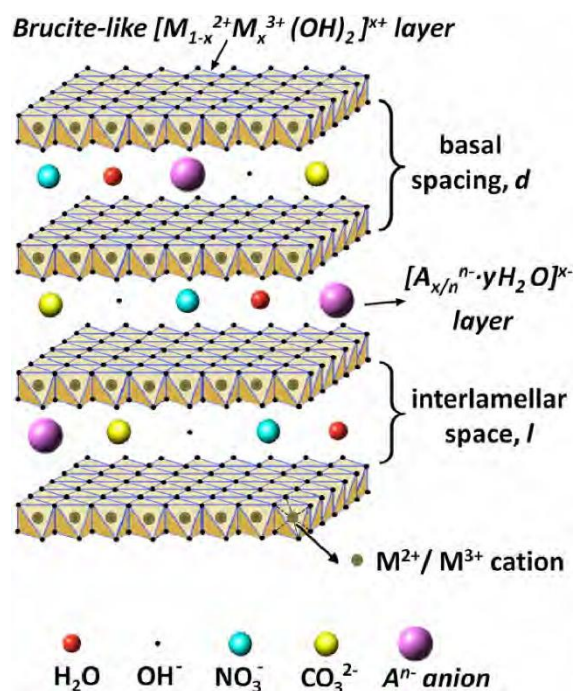

Fig. 2 The demand and the relative percentage for lead salts, metal soaps, organic compounds and organic tins in China (2016 and 2018) and global (2018) (https://www.chyxx.com/)

According to the statistics by Research and Markets (https://www.researchandmarkets. com/), the global thermal stabilizer consumption was 1296 kilotons in 2018, with a high proportion of PVC products containing lead salts, metal soaps, organic compounds and organic tins as follows 47.74 %, 23.80 %, 5.03 %, and 23.43 %, respectively (Fig. 2). With about 46 % globally produced in 2018, China has consumed about 600 kilotons PVC thermal stabilizers. With the expansion of application range of PVC products, the demand for global PVC thermal stabilizers is expected to increase rapidly at a CAGR of around 6 % in a near future. The awareness of the importance for green additives is growing, triggered by the growth of PVC market, leading to a higher demand for low-cost and environment-friendly thermal stabilizers. Due to the high toxicity of lead, the RoHS directive issued in 2003 and the REACH regulations implemented in 2007 by the European Union (EU) control strictly the use of lead salts, and completely banned lead in the EU in late 2015. There is no doubt that the safety of plastic products is of importance because they are closely related to the daily life of people and to their health. However, a large number of lead salts are still produced and used in parts of Asia-Pacific and Africa regions due to the limit of technology and industrial innovation. To date, the development of relative eco-friendly thermal stabilizers such as calcium/zinc

stearate and organic tins is found to inhibit partially the employment of lead salts. It is worth noting that there is also some toxicity in heavy metals in metal soaps such as zinc, barium and cadmium, and metal tin in organic tins. Besides, a class of organic compounds without metal elements, such as phosphite esters, epoxides, polyols, are used with other thermal stabilizers because they do not provide enough stability. Thus, it is greatly significant to develop a novel type of thermal stabilizer of environmentally friendly, non-toxic, reasonable in cost and excellent in performance for the processing and application of PVC. Undoubtedly, this will promote the development of green thermal stabilizers in global market, and prohibit more rapidly the use of lead in the PVC industry, which is also hopefully the general trend of the green sustainable development of the plastic industry worldwide (Tang et al., 2017).

In 1981, the patent reported by Kyowa Chemical Industries of Japan firstly indicated that two-dimensional (2D) layered double hydroxides (LDHs) could significantly improve the performance of PVC composites (Forano et al., 2013; Miyata et al., 1981). Indeed, LDH thermal stabilizers, as a novel eco-friendly PVC thermal stabilizer, have received considerable attention and produced in a large-scale with convenient preparation, yielding to excellent performance, low cost, and non-toxic PVC filler (Xu et al., 2016; Cheng et al., 2011). LDH materials are comprised by a positively charged brucite-like layer in the host layers, and negatively intercalated guest anions in the interlayer region as well as water molecules (Evans et al., 2006). Generally, the chemical formula of LDH materials is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot zH_2O$, where M^{2+} and M^{3+} represent bivalent and trivalent metal cations in the host layers; x is the surface charge and the value of that is determined by the molar ratio M^{3+}: $(M^{2+}+M^{3+})$; A^{n-} represents interlayer inorganic or organic guest anions of charge n; z is the number of water molecules in the gallery (Fan et al., 2014). The typical structure of LDHs is similar to that of brucite ($Mg(OH)_2$) (Scarpellini et al., 2014) (Fig. 3). Up to now, LDHs have been designed by adjusting their chemical compositions, the exchangeable guest anions, as well as by tuning their particle size and controlling their surface properties to address suitable functionality (Taviot-Guého et al., 2018; Feng et al., 2015; Slade et al., 2005; Shao et al., 2015). Such functionalities are of great interest for application, as exemplified by the domain of polymer composites (Gu et al., 2015; Schrijvers et al., 2014), heat retention additives (Guo et al., 2018), ultraviolet absorbents (Wang et al., 2014), flame retardants (Qiu et al., 2018; Gao et al., 2014; Shanmuganathan et al., 2014; Costantino et al., 2005; Zammarano et al., 2005), antioxidant (Feng et al., 2014; Zhang et al., 2018; Zhang et al., 2019) and thermal stabilizers (Aisawa et al., 2019;

107 Shimizu et al., 2017). Lately the interest for functional LDH additives is not fading (Yu et al., 2016;

108 Molefe et al., 2015; Korkusuz et al., 2020). The research progress of LDH thermal stabilizers is here

109 summarized in four parts as 1) thermal stability mechanism, 2) metal composition of host layers, 3)

110 interlayer guests and finally 4) the dispersion state in polymer. The review aims to supply a

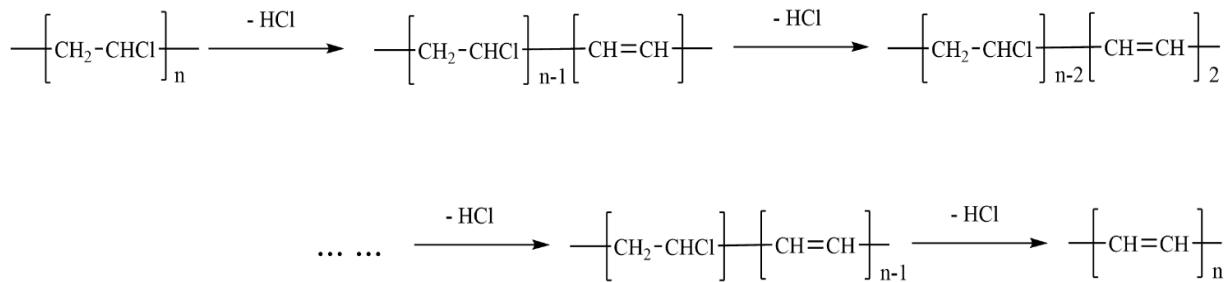111 preliminary understanding of LDH thermal stabilizers.

112

113 Fig. 3 General crystal structure of LDH compounds. Some possible anionic hosts in the interlamellar space are indicated (Scarpellini et

114 al., 2014). Copyright (2014) Elsevier.

115

2. Thermal stabilization mechanism

117

118 PVC resins suffer severely from thermal degradation under temperatures higher than 100 °C and

119 from UV radiation due to the presence of labile chloride ions in the polymer chains. The thermal

120 dehydrochlorination process of PVC is initiated at defect sites and starts to generate C-C double

121 bonds, which activate the subsequent chlorine atoms (e.g., allyl chloride and tertiary chloride

122 structural flaws). Then, the loss of HCl from adjacent units leads to the formation of conjugated

123 bonds into the polymer chains. The conjugated polyene sequence is a chromophore with an

124 undesirable color when the number exceeds six double bonds. Meanwhile, the HCl gas released from

125 the PVC pyrolysis acts as a catalyst and further accelerates the degradation. Thus, the zipper

126 autocatalytic dehydrochlorination process of PVC includes the following two steps (Baum et al.,

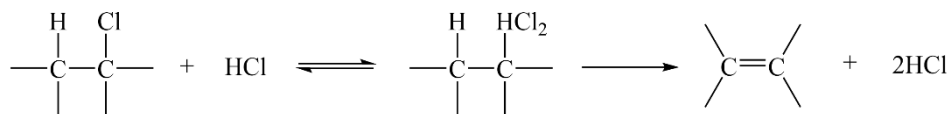127 1958; Wypych et al., 2015; Starnes et al., 2004).

128   (1) The process of PVC autocatalytic dehydrochlorination reaction

$$\left[CH_2-CHCl\right]_n \xrightarrow{-HCl} \left[CH_2-CHCl\right]_{n-1}\left[CH=CH\right] \xrightarrow{-HCl} \left[CH_2-CHCl\right]_{n-2}\left[CH=CH\right]_2$$

129    $$\cdots\cdots \xrightarrow{-HCl} \left[CH_2-CHCl\right]\left[CH=CH\right]_{n-1} \xrightarrow{-HCl} \left[CH=CH\right]_n$$

130   (2) The process of HCl catalytic reaction

$$-\overset{H}{\underset{|}{C}}-\overset{Cl}{\underset{|}{C}}- \;+\; HCl \;\rightleftharpoons\; -\overset{H}{\underset{|}{C}}-\overset{HCl_2}{\underset{|}{C}}- \;\longrightarrow\; \diagdown C=C \diagup \;+\; 2HCl$$

132   Based on the diverse stabilization mechanisms, PVC thermal stabilizers are usually divided into
133   three types: preventive, suppressive and curative thermal stabilizers (Wypych et al., 2018). The
134   removal of HCl is a critical process to inhibit the further degradation of PVC due to the catalytic
135   effect of the HCl gas on the chains propagation reaction. LDHs as inorganic platelets covered by
136   hydroxyl groups, are a class of suppressive thermal stabilizers and enable due to their basicity to
137   retard the PVC degradation by absorbing/neutralizing HCl. The role of LDH additives in absorbing
138   HCl was confirmed experimentally by Ven et al. (2000). The reaction mechanism between LDHs and
139   HCl gas proceeds in two steps (Ven et al., 2000; Yan et al., 2017) (Fig. 4): (1) Based on the
140   exchangeability of interlayer guests, the HCl gas reacted with the interlayer guests of LDHs by
141   exchanging the Cl$^-$ ions into the interlayer and forming the Cl-intercalated LDHs; (2) As more HCl
142   gas is produced, a buffering reaction involves the hydroxyl groups and metal cations forming the
143   layers, leading to a complete destruction of the LDH structure and the formation of metal chlorides,
144   thus preventing the migration of HCl in the entire polymer. In addition, some interlayer guest anions
145   enable to react with the C-C double bonds or active chloride atoms, contributing to further inhibit the
146   autocatalytic degradation of PVC. It is worth noting that, for the step (1), the anions between layers
147   cannot be displaced by Cl ions for the corresponding acids having the similar acid than HCl, such as
148   SO_4^{2-} and NO_3^- (Ven et al., 2000). Subsequently, Wang et al. (2004) proposed that the stabilization
149   mechanism was attributed to the electrostatic interaction between the electron cloud of chlorine
150   atoms in PVC chain and the positive layer charge of LDHs. Such interaction is found to decrease the
151   electronic cloud density of chlorine atoms, thus weakening its activity, and consequently restricting
152   the initiation of dehydrochlorination.

$$\boxed{M^{2+}_{1-x}M^{3+}_x(OH)_2} \quad A^{n-} \ H_2O \quad A^{n-} \ H_2O \quad \boxed{M^{2+}_{1-x}M^{3+}_x(OH)_2}$$

$$\xrightarrow[- H_nA]{+HCl} \quad \boxed{M^{2+}_{1-x}M^{3+}_x(OH)_2} \quad Cl^- \ H_2O \quad Cl^- \ H_2O \quad \boxed{M^{2+}_{1-x}M^{3+}_x(OH)_2} \quad \xrightarrow{+HCl} \quad MCl_2 + MCl_3 + H_2O$$
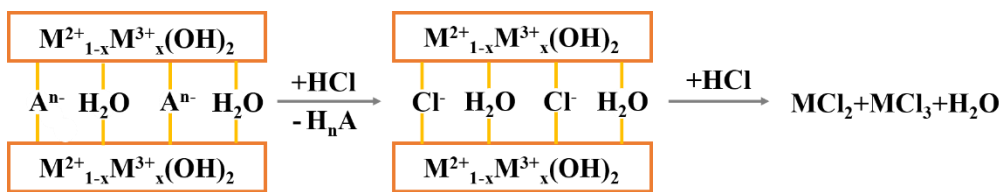
Fig. 4 Schematic illustration for the reaction between the LDHs and HCl gas.

Furthermore, the extent of PVC degradation is generally quantified by the following three ways based on the above mechanism: -The evolution of HCl; -The development of color due to the formation of conjugated double bond sequences; -The change of physical properties due to the crosslinking or cleavage of the polymer chains. The challenge is to protect PVC from its degradation, so part 2 on the possible reaction and mechanism known.

3. Adverse effects of heavy metals in PVC thermal stabilizers

Until now, the traditional PVC thermal stabilizers are generally composed of heavy metallic compounds. To protect PVC from is degradation, heavy metals are incorporated to react with HCl or unstable chlorine present in PVC chains. However, heavy metal pollution is one of the most dangerous issues among the current environment contaminations because of their persistent nature, toxicity, tendency to accumulate in organisms and their non-degradability. So far, it has spread broadly over the globe through industrial effluents, organic wastes, refuse burning, and transport, perturbing the environment and ultimately posing serious health hazards to humans (Rai et al., 2019; Li et al., 2018; Khan et al., 2015). Heavy metals mainly refer to a kind of metals with atomic density of over 5 g/cm^3, but depend on their chemical properties. Among these, certain metal elements (e.g., Cu, Fe, Ba, and Zn) are essential microelements in human body, which are beneficial at low level but become hazardous when they exceed the limited concentration, and others (e.g., As, Pb, Cd, and Hg) have totally no favorable role in humans and can be noxious to health even at low concentration (Sankhla et al., 2016). To a great extent, the toxicity of heavy metals is caused by the chemical reactivity of the ions with cellular structural proteins, enzymes and membrane system. For example, they combine with protein sites which are not produced for them, replacing original metals from their natural binding sites, leading cells to malfunction and then to poisoning (Mohod et al., 2013; Mohammed et al, 2011). Besides, heavy metal ions are inclined to accumulate in vital organs such as brain, heart, liver and kidney, disturbing normal metabolomics and blocking the crucial activities in body (Mahurpawar, 2015). Although the perilous effects of heavy metals have aroused much

awareness, the exposure risks to heavy metals continues to increase in many parts of the world. For example, a majority of metals in PVC thermal stabilizers belong to heavy metals, such as lead in lead stabilizers, tin in organic tins, zinc, barium and cadmium in metal soaps. With a large amount of PVC products applied to chemical, automobile, construction, packaging, and other industries, the heavy metals in PVC stabilizers are possibly migrating into human body through drinking water, packaged food, and even air, causing bio-toxic impacts on health. For further understanding the necessity of green PVC thermal stabilizers, the adverse effects of some common heavy metals in traditional PVC products on human health have been presented briefly below.

3.1 Lead

Lead (Pb), a class of hazardous heavy metals, is harmful even at extremely low amounts for humans. It has both acute and chronic influence on human body based on content and exposure level. Generally, most of the lead entering into our bodies can be eliminated timely through urine, but it also has risks of accumulation, especially for children (Mishra et al., 2018). Nowadays, a blood lead reference value over 50 µg/L is used to identify children who have more lead in their blood than most children, supported by Centers for Disease Control and Prevention (CDC). High levels of lead in the body result in irreversible damage to the internal organs, the central nervous and cardiovascular system. It will simultaneously affect the behavior and learning ability of people, such as hyperactivity, memory decline, impaired concentration, dysgenesis, hypertension, slowed growth, dyspepsia, and muscle and joint pain (Jaishankar et al., 2014). Thus, lead is regarded as the biggest health threat to children because the damage of lead poisoning will last a lifetime. Studies show that lead poisoning can stunt children's growth and injure the nervous system as well as cause learning disorder, even have relation to children's crime and anti-social behaviour.

3.2 Cadmium

Cadmium (Cd) is a common heavy metal with serious harmfulness for health. The negative effects of Cd have been observed on a variety of organ systems, mainly including liver, kidneys, lungs, brain and bones (Zahra et al., 2017). High exposure may irritate the stomach by ingesting and cause lung damage by inhaling, and then damage the brain and kidneys. The principal manifestation

of the clinical symptoms is nausea, vomiting, diarrhea, dyspnea and muscular weakness. Besides, cadmium poisoning is also linked with bone diseases due to the buildup of Cd in the kidneys, e.g., osteoporosis, osteomalacia, spontaneous fractures, even leading to myocardial dysfunction and hypertension. It's worth noting that the most notorious case, «itai-itai» disease in Japan, the large-scale Cd poisoning, aroused the world's attention about the damage of Cd element. And it shows a high correlation between the incidence of itai-itai and the level of cadmium pollution (Engwa et al., 2019).

3.3 Tin

The toxicity of heavy metal tin has little threat to human health. Up to now, tin is defined as an essential minor element for men. Especially, the most inorganic tin compounds can leave human's body rapidly without causing harmful effects, even high-level intakes only can lead to skin rashes, stomachaches, nausea, vomiting, diarrhea, abdominal pain, headache, and palpitations according to the study. Conversely, organotin compounds, served as PVC thermal stabilizer, have an enormous threat on human health(Ostrakhovitch, 2015). They easily cross the blood-brain barrier and placenta, and bio-accumulate in the bone, liver, kidney, and lung. People suffer from dermatosis, visual abnormalities, respiratory difficulties, and gastrointestinal and neurological disorders when they have a short-term exposure to large amounts of organotin compounds. Based on reports, certain neural injury can exist for many years, and there are some fatal cases after organotin compounds poisoning.

3.4 Zinc

Zinc has bio-importance as an essential trace element in human body. In general, it is supposed to be a kind of basically non-toxic heavy metals which can be taken orally. Interestingly, both zinc deficiency and excess have different adverse impacts on human health (Okereafor et al., 2020). For instance, the former one can cause anemia and retardation of growth and development; the later one leads to system disorder and then impedes growth and reproduction, and the clinical symptoms of zinc excess (also known as zinc poisoning) consist of vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, and kidney failure, similar like that of lead toxicosis which is easily be mistakenly diagnosed as lead poisoning (Singh et al., 2011). In addition, zinc plays an

important role in regulating the cell growth and death. Its excess and deficiency both cause apoptosis. Studies have shown that there may be a connection between zinc imbalances and some disease, e.g., Alzheimer's disease, diabetes.

3.5 Barium

Barium is considered as a heavy metal due to its chemical property though its atomic density is less than 5 g/cm^3. Ba exposure can be divided into acute ($<$14 days), intermediate (15-364 days), or chronic ($>$1 year). The most common toxicity hazards usually cover heart disease, kidney failure, pneumonedema, respiratory paralysis, and gastrointestinal bleeding (Kravchenko et al., 2014). In particular, short-term exposure can bring in vomiting, anxiety, diarrhea, dyspnea, facial paralysis, and myasthenia. A mass of barium intakes can cause high blood pressure, cardiac arrhythmia, paralysis, hepatorenal failure, and possibly death. Moreover, no studies show that there are association between barium toxicosis and cancer so far (Oskarsson, 2015).

4. The interest of LDH layers

To overcome the issue of toxicity shown in the previous part, environmental-friendly LDHs are more and more considered as a filler for PVC. Indeed, pioneer researches demonstrate their efficiency in neutralizing HCl, reacting with unstable Cl and conjugated double bonds in polymer chains, playing a crucial role in restraining PVC degradation.

4.1 Importance of layers dispersion and distribution

As mentioned above, the mechanism of LDH thermal stabilizers to improve the stability of PVC resins consists of two-step process: firstly, the interlayer anions react with HCl gas and secondly, the LDH layers react with HCl, to form metal chlorides. Thus, the interlayer anion guests and host layers have both an important to absorb HCl. However, LDH particles as inorganic fillers have a strong tendency to agglomerate, that causes usually their insufficient dispersion state into polymer. Indeed, the dispersion of LDH additives in polymer is one of the critical factors not only regarding the HCl-absorption for PVC but also all polymer LDH composites. The uniform dispersity of LDHs in

resins allows a sufficient amount of LDH particles per unit volume of polymer composites to get an efficient absorption of HCl, and to maintain the thermal stabilization of LDHs (Singh et al., 2018; Kango et al., 2013). In general, the particle size and surface nature of inorganic fillers have a significant impact on the compatibility between additives and polymer, thereby the dispersion state of LDH particles in resins may even increase the mechanical properties of PVC. Thus, a lot effort is paid to adjust the size and to modify the surface of LDHs to optimize their dispersion state in resins as follows in the next parts.
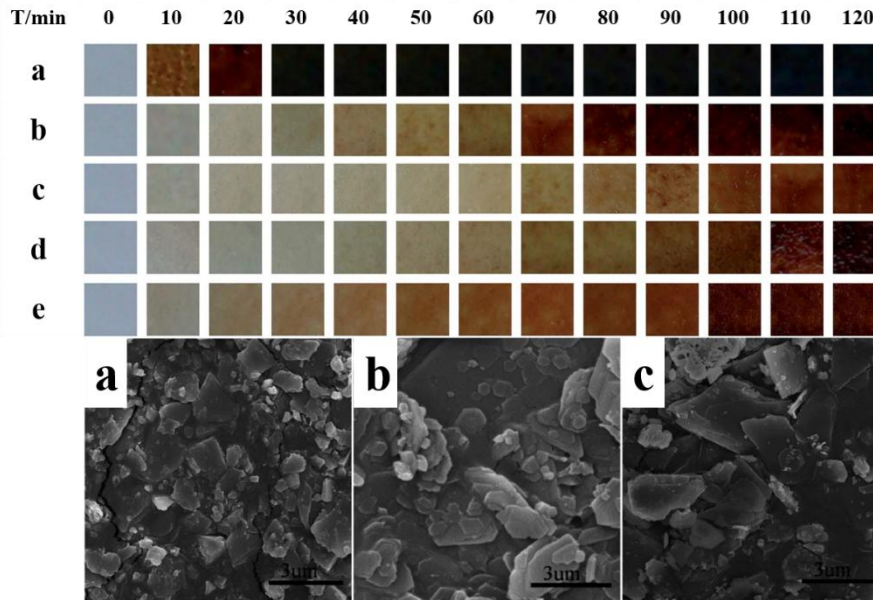
4.1.1 Control of particle size and particle size distribution

Previous studies report that LDH particles with small size and narrower size distribution are well dispersed in PVC/LDHs composites. Chemical and/or technological processes are applied to control size and size distribution as exemplified with separate nucleation and aging steps (SNAS) method, hydrothermal synthesis method and ammonia-releasing method). It is possible to adjust the reaction conditions (e.g., reaction time, temperature and concentration, etc.) to control precisely the particle size in the range from nanometer to micron with the narrow size distribution, thus broadening the possible application of LDHs as filler for polymer (Theiss et al., 2016; Zhao et al., 2002; Xu et al., 2006; Oh et al., 2002; Qiu et al., 2018).

For example, Wen et al. (2015) synthesized a series of green CaAl-LDHs with different particle sizes using $Ca(OH)_2$, $Al(OH)_3$ and Na_2CO_3 by adjusting reaction times and crystallization times. SEM images show an example of sample prepared with a precise reaction time and crystallization time with high purity and crystallinity as well as displaying regular crystal form (Fig. 5a-c). The color change associated to this PVC composite presents the longer aging time (Fig. 5d). This shows that the small particle size with narrow distribution is beneficial for LDH filler to promote the thermal stability of PVC composites.

Based on the above work, the research group at BUCT fabricated a series of $MgAl-CO_3$-LDH of size from 202 to 334 nm using $Mg(OH)_2$, $Al(NO_3)_3 \cdot 9H_2O$, and light magnesium carbonate (LMC) as starting materials, and studied the influence of different-sized LDH particles on thermal stability property of LDHs/PVC composites. The order of induction time of HCl evolution for LDHs/PVC composites is reported in Fig. 6. It shows as a function of the particle size a small induction time for tiny particles that is optimized for a particle size of 220 nm then it is found to decrease again (Fig. 5).
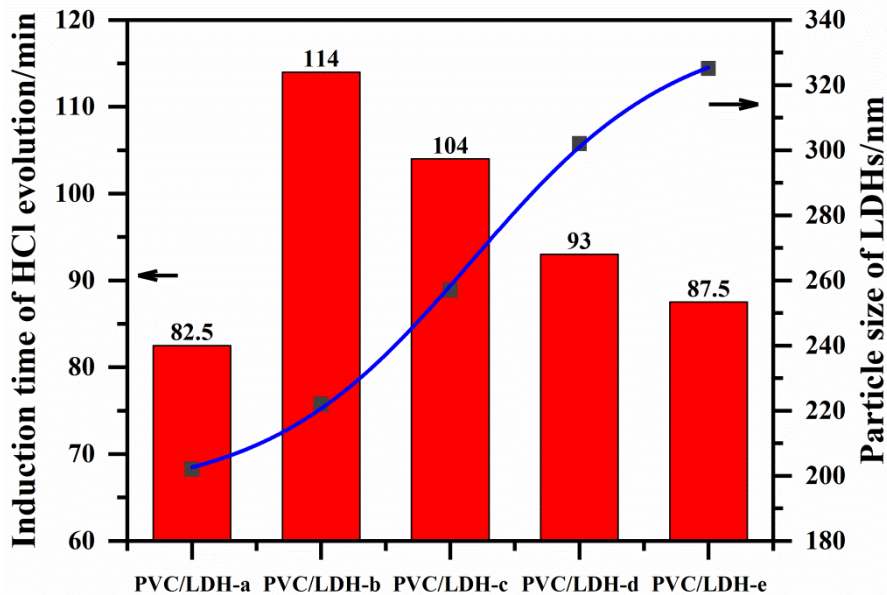
It is probably due to the fact that the sample of very small particle size (LDH-a) is inclined to agglomerate, affecting the dispersion of particles into PVC, while the LDH filler of larger size than 220 nm (LDH-b) exhibits lower compatibility with PVC. This work further demonstrates that the particle size of stabilizers plays a key role in improving the thermal stability of PVC by influencing the dispersion state of LDH platelets in PVC.

Fig. 5 (a-c) SEM images of hydrocalumites prepared with different reaction time and crystallization times; (d) Effect of hydrocalumites prepared with different reaction time and crystallization time on the stability of PVC at 195 ± 1 °C. Reprinted with permission from (Wen et al., 2015). Copyright (2015) The Royal Society of Chemistry.

Besides, different synthesis methods are available to tune the particle size of LDH platelets. A Chinese patent reports a method for preparing LDHs in a rotary liquid membrane reactor, this is found to improve the nucleation rate and reduce the crystal growth rate. The LDH particle size are small ranging from 10 to 150 nm with a narrow particle size distribution range (20-50 nm), this should be beneficial to disperse LDH particles into PVC (Lin et al., 2012). The LDHs prepared by the above method supplies a good initial stability and increases the initial whiteness of PVC products (Zhang et al., 2018). Later, another two Japanese patents report that the LDH particles with small particle size improve both the thermal stability and transparency of PVC resins. Stabilized as a suspension, small particles do not aggregate, leading to their efficient dispersion (Kurogi et al., 2013; Nosu et al., 2017). For the aggregation of LDHs when using smaller particles occurring during both drying process and long-term storage in suspension, it was proposed to improve the dispersion state of LDHs by reducing the lattice distortion of (*003*) direction to $3*10^{-3}$ or less and adjusting the particle size of LDHs in the range from 5 to 200 nm (Mori et al., 2018). Besides, the HCl-absorption

328 ability of LDHs was increased five times to that of calcium stearate by further controlling the particle

329 size and specific surface area of LDHs (He et al., 2017). Interestingly, a Chinese patent developed a

330 novel method for synthesizing LDH thermal stabilizer with controllable diameter-thickness ratio, and

331 the effect of these ratio against the thermo-stabilization property of PVC composites, this from the

332 initial and the long-term stability of PVC/LDH composites (Song et al., 2019).

333

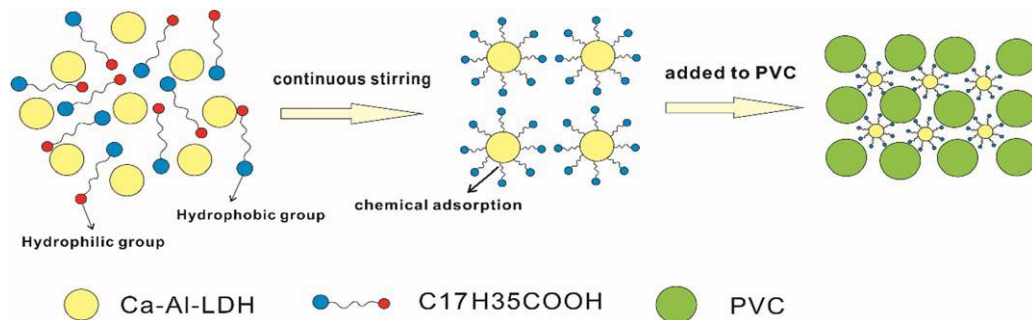334 Fig. 6 Effect of particle size of LDHs on the induction time of HCl evolution.

335

4.1.2 Surface modification of LDHs

337

338 To design efficient organic-inorganic composites, a crucial problem is that the inorganic

339 additives tend to agglomerate easily together in diverse organic solvents. Altering the surface

340 properties of inorganic fillers from their balance hydrophilicity versus hydrophobicity by chemical

341 treatments appears often as a useful way to improve their compatibility and dispersion as well as the

342 interfacial interactions with polymer segments, thus further facilitating LDH platelets to be integrated

343 (Kotal et al., 2015; Gao et al., 2020). Generally, the surface of LDHs is organically modified by the

344 methods shown below: (1) Their surfaces could be modified by organic surfactants so called

345 «organo-modified», thus generating a strong repulsion between LDH particles, decreasing their

346 aggregation behavior, anionic surfactants such as stearate, alkyl carboxylates, polyol, sodium oleate

347 are commonly used (Song et al., 2008; Miyata, 1987; Mitamura et al., 2018); (2) Preparing

348 PVC/LDHs composites by solution mixing method is an alternative route to modify the LDH surface

349 with organic solvents and to promote the interfacial reaction between LDHs and PVC resins.

350   One end-group of organic surfactants is usually hydrophilic, this connected to the hydroxyl

351   groups of LDH layers, while at the other end is present a hydrophobic group, helping the filler to be

352   dispersed into polymer. Indeed, the use of surfactant is the common route to modify the platelets

353   LDH surface, render it hydrophobic and organophilic towards polymer chains as well as to expand

354   strongly the basal spacing. The school-case with zinc stearate-intercalated MgAl-LDHs shows an

355   increase in the interlayer spacing of LDHs, making possible for the inside layer region of LDHs to

356   react more easily with HCl gas, and in the same time helping to disperse the platelets in polymer

357   (Wang et al., 2017). Moreover, Liu et al. (2008) using a series of intercalated MgAl-LDHs with

358   interlayer anions of nitrate (NO_3^-), dodecyl sulfate ($C_{12}H_{25}OSO_3^-$, DS^-) and stearate ($C_{17}H_{37}COO^-$, St)

359   show that LDH-St sample stabilizes better PVC than the others. Three reasons may explain such

360   behavior: (1) the size of DS^- and St ions is much larger than that of NO_3^- ions, with the hydrogen

361   bonds between interlayer guests and layer hydroxyl groups more weakened; (2) dodecyl sulfate and

362   stearate anions as organic surfactants to fully compatibilize LDHs platelets with PVC chains; (3)

363   stearate anion is known as a PVC thermal stabilizer, reducing the thermal degradation of PVC. In a

364   step further, a Chinese patent report the use of a modified silica core-shell particles into the interlayer

365   gallery of MgAlZn-LDHs to produce a novel modified LDH thermal stabilizer, which is found to

366   facilitate the compatibility of LDHs with PVC resins and to enhance their long-term stability (Shen

367   et al., 2017).

368

369   Fig. 7 Schematic illustration for the modification of CaAl-LDHs by sodium stearate. Reprinted with permission from (Yang et al., 2018).

370   Copyright (2018) John Wiley and Sons.

371   Concerning the intercalation of organic guests, a straightforward route is to mix LDHs platelets

372   and the suitable organic molecules, letting the latter being tethered to LDH layers surface. For

373   instance, Yang et al. (2018) modified the surface of LDHs only in absence of intercalated stearate (St)

374   anions into the LDH interlayer. The color tests using thermal exposure and Congo test show longer

375   time of degradation when using the surface-modified ST-LDHs compared to pure PVC or PVC

376   layers with unmodified LDHs. It is explained by the stearate anions coated onto the surface of LDHs

377 tethered to hydroxyl groups through electrostatic interaction with their carboxylate end-group leaving

378 the long-alkyl chains dangling outside and facing PVC chains, thus enhancing the dispersion of

379 inorganic additives into polymer (Fig. 7). For instance, epoxidized soybean oil can serve as a

380 modifier and dispersant to prepare surface-modified MgAl-LDHs, and it can avoid the aggregation of

381 LDH particles with the epoxy groups interacting with abundant hydroxyl groups of the LDH layers,

382 thus facilitating the compatibility of LDH additives with PVC resins (Zhou et al., 2018).

383   Similarly, Bao et al. (2006) modified the surface of nano-sized LDHs with alkyl phosphonate,

384 and found that the PVC/LDH composites presented an enhanced thermal stability and a significant

385 increase of the dehydrochlorination time. Liu et al. (2009) grafted toluene-2, 4-di-isocyanate (TDI) to

386 the hydroxyl groups of the LDHs platelets surface, and the resulting PVC/LDH-TDI composites

387 show enhanced thermal stability, this explained by the grafting between the hydroxyl groups of

388 LDHs and TDI through covalent-bonding. Furthermore, Zhou et al. (2017a and 2017b) utilized

389 polyethylene glycol and cyanurate (or uracil) to organo-modify LDHs. Polyethylene glycol (PEG)

390 exhibit superior compatibility with LDHs, and when coated onto the LDHs platelets, they avoid LDH

391 particles to agglomerate. Cyanurate (or uracil) molecules, as thermal stabilizer, interact with the

392 hydroxyl groups, stopping the influence of emulsification by PEG. The synergistic effect between

393 two modifiers helps to control the LDH particles size with a uniformly dispersed state in resins.

394 Interestingly, Zhang et al. (2016) prepared MgAl-LDHs with addition of ammonium compounds and

395 urea, and found that the presence of NH_4Cl or $CO(NH_2)_2$ improved the compatibility between LDHs

396 and PVC, as visualized by SEM analysis. The color of PVC/MgAl-NH_4Cl-LDH and

397 PVC/MgAl-$CO(NH_2)_2$-LDH composites turned brown after 60 min and 70 min, respectively, both

398 slower than that of MgAl-LDHs, suggesting the beneficial effect of the uniform LDHs layers

399 dispersion on the thermal performance of PVC.

400

401 Fig. 8 TEM micrographs of (a) 5 wt% PVC/LDH-DS nanocomposite and (c) 5 wt% PVC/LDH-St nanocomposite. Reprinted with

402 permission from (Liu et al., 2008). Copyright (2008) Elsevier.

The traditional polymer processing of PVC composites is using a double roller machine under high temperature, named as melt blending method from the mixing of all additives with polymer. Unfortunately, the drying process needed before melt mixing leads often the particles to aggregate. Thus, the dispersion of the inorganic fillers in polymer appears a difficult task for this method. For this reason, solvent blending method, one used for the blend of different types of polymers, also has been applied for polymer/filler composites since 1990s, also called by solvent mixing/intercalation method (Alexandre et al., 2000). Wang et al. (2002) first prepared the PVC/clay nanocomposites by solution blending method using tetrahydrofuran (THF) as the solvent. Thermal decomposition and mechanical properties of composites were increased with the formation of mixed immiscible-intercalated system. Subsequently, a novel facile preparation of PVC/LDH composites via solution intercalation method has been reported by Liu et al. (2007) using THF and cyclohexanone as solvents to exfoliate LDH into nanometer scale and uniformly dispersed in PVC. The nano-sized LDH platelets well-dispersed in polymer could provide more pathway to diffuse the HCl gas (more tortuosity), leading to the significant improvement of the thermal stability. Also, Liu et al. (2008) prepared PVC/DS-LDH and PVC/St-LDH composites by the same route. TEM images (Fig. 8) showed LDH particles well exfoliated/isolated at the nanometer scale and homogeneously dispersed in PVC matrix. This results into an enormous interface area as well as a strong interfacial interaction between PVC and LDHs. This strongly supports that the solution intercalation method promotes the uniform dispersity of LDH particles in polymer (Moyo et al., 2008).

Since the HCl-scavenging ability of LDHs performs the best by increasing the thermal stability performance of PVC composites only with LDH particles well dispersed in PVC resin, it is crucial to gain in the stability of PVC resins to add LDHs suitably modified to act as a long-term thermal stabilizer.

4.2 Importance of metal composition in LDH layers

The surface of LDH layers is alkaline, consisting of hydroxy groups, and LDH thermal stabilizers could absorb effectively and neutralize HCl gas generated from the degradation, acting as a buffer to improve the thermal stability of PVC. The properties of LDH layers are influenced by the metal compositions. Therefore, the possibility to tune the metal composition of LDHs can further enhance the HCl absorption ability or promote the coordination with active Cl^- anions. This is
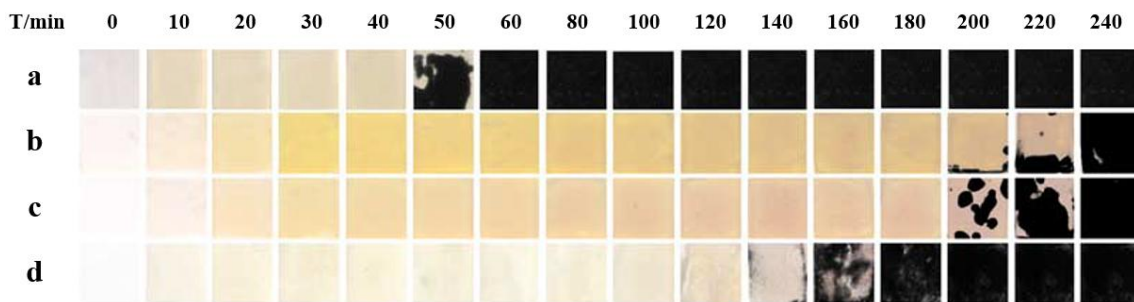
exemplified by selecting metal cations and tailoring the layer and interlayer compositions to optimize the stability of LDHs (Yu et al., 2017; Labuschagné et al., 2019). MgAl-LDHs is the most commonly used LDH thermal stabilizer, and there are two main routes to further raise the performance of LDHs: (1) The introduction of metal cations with stronger electronegativity such as Zn^{2+}, Cu^{2+} enables to decrease the interaction between hydroxyl group and host layers as well as promote the reaction between hydroxyl group and HCl gas; (2) Doping rare earth metals (e.g., Ce^{3+}, La^{3+}) into the LDH layers can coordinate with active Cl atoms in polymer chains by electrostatic attraction.

4.2.1 Incorporation of metal elements with higher electronegativity into LDH layers

The chemical properties of LDHs are adjusted by tuning the composition of metal cations of the host layers in a certain range. Until now, MgAl-LDHs have been mostly widely used as thermal stabilizers. Since Kyowa Chemical Industries of Japan patented the enhancement of MgAl-LDHs on the thermal stability of PVC in 1981 (Miyata et al., 1981), the next investigations were further focused on the impact of the species and molar ratio of metal cations in LDH layers on the stability of LDHs.

Fig. 9 Thermal stability of (a) PVC reference and samples of PVC containing (b) MgAl-CO_3-LDH, (c) MgZnAl-CO_3-LDH and (d) MgZnAl-maleate-LDH. Reprinted with permission from (Lin et al., 2006). Copyright (2006) Elsevier.

The cation substitution of metal elements of higher electronegativity than Mg^{2+} decreases the electronegativity of the layers, thus weakening the interaction between the host layers and the hydroxyl groups with a reactivity improved. Meanwhile, metal cations of larger ion radius than Mg^{2+} will decrease the M-O bond strength with the longer bond distance, thus weakening the interaction between hydroxyl groups and the interlayer ions. It is presumed that the substitution of metal elements with the above characteristics can increase the HCl absorption capacity of LDHs, thus optimizing the thermal stability of PVC. For instance, the electronegativity of zinc is 1.65, higher than that of magnesium (1.31) and aluminum (1.61), and its ionic radius is 0.74 Å, a little larger than

461   Mg^{2+} (0.65 Å) (Slade et al., 2005). Comparatively, the substitution of Mg^{2+} by Zn^{2+} cations in LDH

462   layers might be beneficial to enhance the thermal stability of LDHs in resins (Kuroki et al., 2016;

463   Lee et al., 2016). Lin et al. synthesized Zn-substituted series MgAl-LDHs with Mg: Al: Zn molar

464   ratios of 3.0:2.0:1.0 (Lin et al., 2006). Pure PVC sample presents a poor thermal stability and turns

465   completely black after only 40 min at 180±1 °C, while the stability time of PVC/MgAl-LDH

466   composite is clearly enhanced with the onset of blackening delayed to over 180 min. Interestingly,

467   MgZnAl-LDHs improve even more the thermal stability of PVC composites than MgAl-LDHs,

468   especially the initial coloring (Fig. 9). This demonstrates that the substitution by Zn^{2+} cations

469   improve the thermal stability of PVC due to the higher electronegativity and larger ion radius.

470   Besides, it is worth noting that Zn^{2+} cations can also inhibit the formation of conjugated polyene

471   chains by replacing allyl chloride, explaining the reason why MgZnAl-LDHs fillers improve

472   significantly the early coloring and transparency of PVC sheets (Dong et al., 2019). In another step,

473   the maleate anions are incorporated into MgZnAl-LDHs, and the same authors show that the hybrid

474   phase further improves the stability of PVC through its early coloring delayed but its long-term

475   stability slightly reduced (see part 4.3).

476   Similarly, copper-containing LDH compounds might be considered as an effective smoke

477   suppressant for PVC (Chen et al., 2018). The electronegativity and ion radius of Cu is 1.90 and 0.72

478   Å, higher than that of Mg, thus it is interesting to investigate how the copper-containing LDHs affect

479   thermal behavior of PVC resins. For instance, Zhu et al. (2011) employed the urea hydrolysis method

480   to produce copper-containing MgAl-LDHs. It was found in Congo red tests (Fig. 10) that the stability

481   time of pure PVC was only about 6 min, that of PVC/MgAl-LDHs greatly increased to 18 min, and

482   that of PVC/MgCuAl-LDHs reached 30 min. The MgCuAl-LDH product presents the best thermal

483   stability behavior in PVC resins among the series, and the incorporation of Cu^{2+} cations significantly

484   enhanced the stability time of PVC/MgAl-LDH composites by over 50%. This further proves that the

485   addition of bivalent metal elements of larger ion radius and stronger electronegativity contributes to

486   improve HCl scavenging ability of LDHs. In addition, another reason for the improvement of

487   stability time of MgCuAl-LDHs is that Cu^{2+} ions act as a reductive coupling agent facilitating the

488   generation of crosslinks from allylic chlorides on adjacent polymer chains during the PVC thermal

489   degradation process. Such cross-linked networks protect the polymer chains against thermal

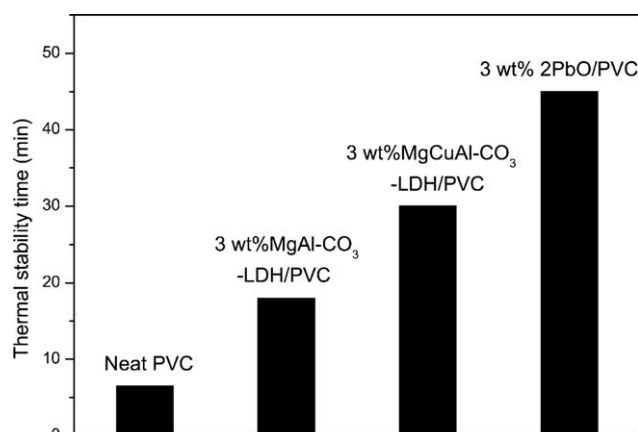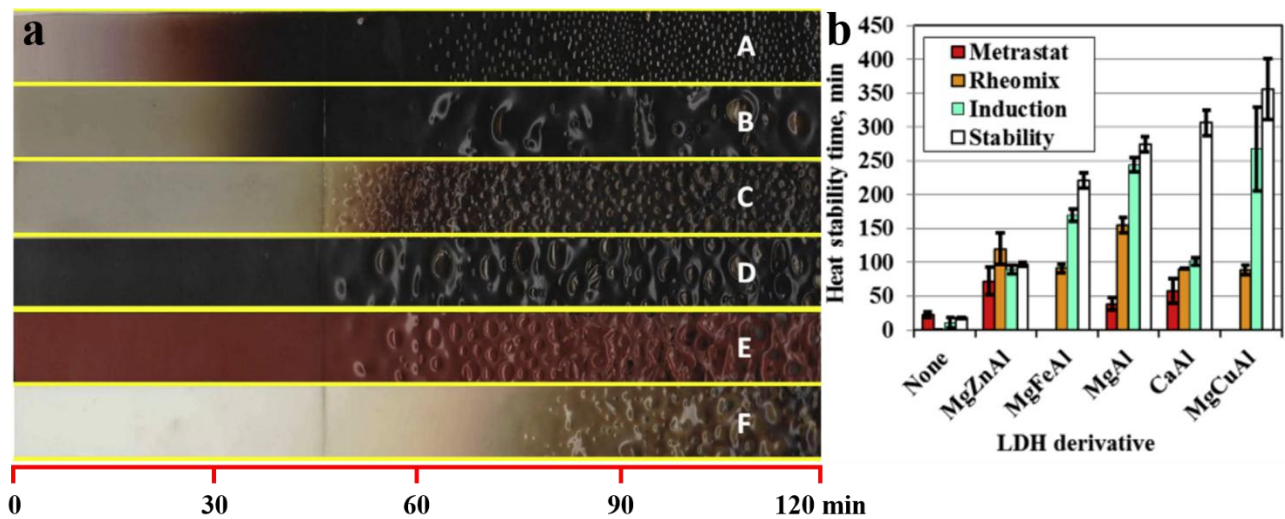490   decomposition, even in the dehydrochlorination process.

Fig. 10 Thermal stability time of neat PVC and its composites containing lead salts, MgAl-CO$_3$-LDH and MgCuAl-CO$_3$-LDH measured by Congo red tests. Reprinted with permission from (Zhu et al., 2011). Copyright (2011) John Wiley and Sons.

A recent example of such cation substitution in LDH layers was reported by Labuschagné and co-workers (2015), by substitution between Zn^{2+}, Fe^{2+}, Ca^{2+} and Cu^{2+} cations to produce MgMAl-LDHs (M=Zn, Fe, Ca and Cu) using metal oxides or hydroxides as the starting materials. The performance of PVC/LDH composites was studied as a function of the LDH fillers under various test conditions (Fig. 11). Here, for PVC composites, Metrastat corresponds to a method using the static thermal stability testing in the oven at 200 °C, and Rheomix refers to the dynamic thermal stability testing using the torque rheometer technique at 200 °C. Induction and stability refer to the change in time of the conductivity in water using due to the released HCl gas when PVC composites decompose at 200 °C, among these, the induction time is required to reach the inflection point in the conductivity curve, the stability time is the time until a conductivity difference of 50 μS cm^{-1} is reached. This demonstrated that the conventional product MgAl-LDHs presents the best behavior in dynamic thermal stability tests, however, MgZnAl-LDHs greatly improved the color retention with a longer stability time, 72±20 min in static thermal stability tests. MgCuAl-LDHs provided the better HCl absorption ability, delaying the release of the volatile gas for a longer time in the conductivity evaluation (Indeed, the progress of the decomposition is followed by measuring the change in the conductivity of the water as for the measurement for pH, shown in Fig. 12). Considering the color of Fe^{3+} and Cu^{2+} ions, MgFeAl-LDHs and MgCuAl-LDHs are only suitable for the dark PVC products. Conversely, MgZnAl-LDHs displayed the superior initial coloring and transparency in the series, thus of interest in practical applications. Besides, a patent reports LDH stabilizer using the quaternary cation composition MgZnCaAl-LDHs, which can react with HCl formed by PVC degradation to generate $MgCl_2$, $ZnCl_2$, $CaCl_2$, and $AlCl_3$, respectively (Ishvarlal et al., 2018). Zinc element presents a positive influence on the initial period to stabilize PVC but also a negative effect
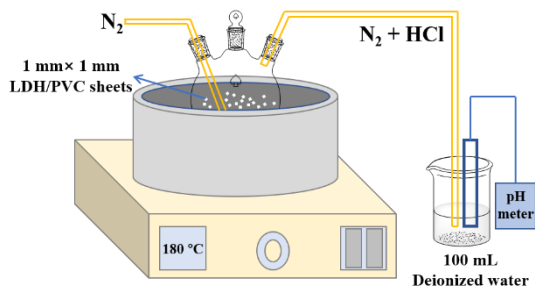
516 on the long period because the $ZnCl_2$ product promotes PVC decomposition. The preparation of

517 quaternary LDHs can utilize the advantage of Zn element and avoid the drawback of $ZnCl_2$ due to

518 the synergetic effect between four metal elements. To sum up this part, the cation substitution is of

519 interest as observed by the thermos-stability tests, and it is possible to finely tune the composition to

520 obtain LDH thermal stabilizers with optimal performance in specific tests and practical applications.

521

522 Fig. 11 (a) Metrastat sample appearances. (A) Neat PVC; (B) MgAl-LDH; (C) CaAl-LDH; (D) MgCuAl-LDH; (E) MgFeAL-LDH,

523 and (F) MgZnAl-LDH; (b) Static and dynamic heat stability times measured at 200 °C using the torque rheometer technique

524 (Rheomix), following the development of color with heating time (Metrastat), and tracking the evolution of hydrochloric acid

525 (Thermomat induction and stability times). Reprinted with permission from (Labuschagné et al., 2015). Copyright (2015) Elsevier.

526 The composition of LDH layers can also be varied by adjusting the molar ratios between

527 divalent and trivalent cations, that may affect the thermal stability of PVC. The variation of the metal

528 molar ratio within the layers results in the change of the charge density of the layers and

529 consequently it may influence the interaction between interlayer guests and host layers, and thus the

530 possible uptake of Cl⁻ anions into the interlayer galleries. Furthermore, the variation in the cations

531 molar ratio changes the electronegativity, thus affecting the interaction between cations and the

532 hydroxyl groups, thus most probably changing the HCl absorption capacity and the thermal stability

533 of LDHs. For example, Lin et al. (2005) prepared a series of MgAl-LDHs with different Mg: Al

534 molar ratios by a method involving separate nucleation and aging steps. Thermal aging tests showed

535 that the thermal stability of PVC became worse with the increasing Mg: Al molar ratio and the

536 optimal molar ratio of Mg: Al was found to be 2: 1. The results could be explained by two reasons: -

537 the charge density of the layers decreased with increasing Mg: Al molar ratio, thus the driving force

538 for up-taking Cl⁻ into the interlayer galleries is reduced; - an increase in Mg^{2+} cations of lower

electronegativity weakens the reaction activity of layer hydroxyl groups towards HCl gas. Both points are detrimental to absorb HCl by LDH layers and accelerate the PVC autocatalytic decomposition.

Fig. 12 Schematic diagram of dehydrochlorination test equipment.

As an effective chloride adsorbent, the enhancement of zinc element on the thermal stability effect of LDHs has been proved, however, the long-term stability performance of ZnAl-LDHs in PVC are unsatisfactory. Larger amount of Zn element results in the "zinc burning" phenomenon because the undesirable product $ZnCl_2$ can catalyze the PVC degradation, leading to the strong degradation of PVC suddenly turning black. Thus, it is necessary to regulate the molar ratio of Mg: Zn: Al in an appropriate range to improve the stability performance of LDHs. For instance, Wang et al. (2013) synthesized a series of MgZnAl-LDHs with the molar ratio of M^{2+}: M^{3+} = 2 and diverse molar ratio of Mg: Zn. This demonstrated that the thermal stability of PVC sheets increased as a function of Zn^{2+} cation content, with Mg: Zn = 1.0 presenting the optimal thermal stability. It suggested that the higher electronegativity and ionic radius of Zn element weaken the interaction between the host layers and the layer hydroxyl groups as well as the interaction between hydroxyl groups of layers and guest anions, facilitating the hydroxyl groups to react with HCl.

4.2.2 Incorporation of rare earth elements into LDH layers
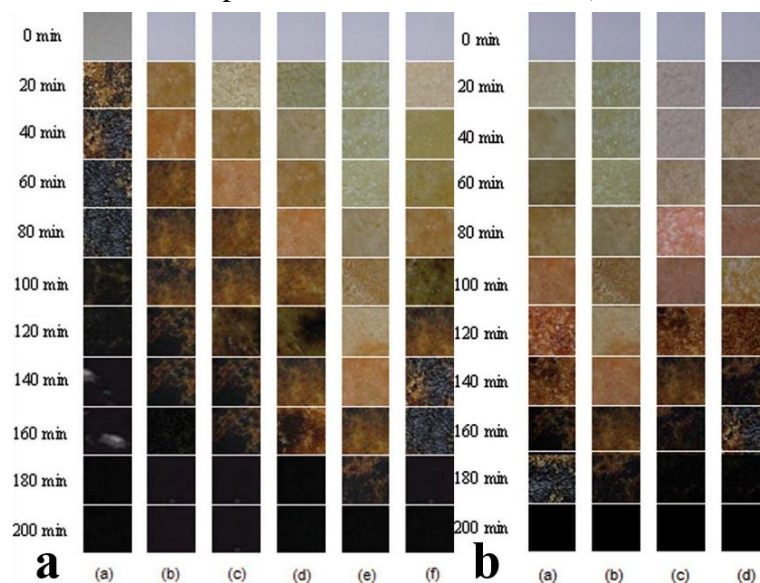
Rare earth thermal stabilizers have a great research potential with non-toxicity, high-efficiency, and a good synergetic effect with other stabilizers. Rare earth (R.E.) metals enable to serve as central cations to receive lone pair electrons on their empty orbitals and their cations have large ion radius. Theoretically, R.E. cations should directly react with unstable chlorine atoms and HCl gas to form a stable coordinate complex, preventing the growth of " polyene structure", as well as to be combined with stabilizers to improve their compatibility in PVC. Besides, R.E. cations may increase the activation energy of PVC thermal dehydrochlorination reaction by capturing free radicals, slowing

down the degradation rate (Zhang et al., 2017; Zhang et al., 2014). Thus, an enticing approach is to combine LDHs and R.E. elements to further optimize the thermal stability of LDHs in PVC by doping rare earth cations (RE^{3+}) into LDH host layers.
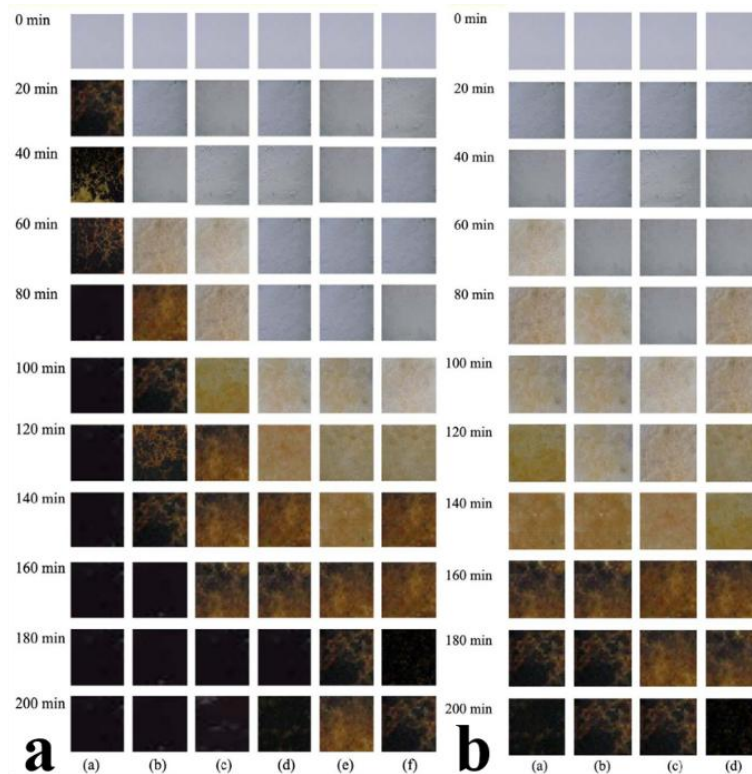
Using MgAlCe-LDHs and ZnAlLa-LDHs as filler with varying molar ratios of RE^{3+}: Al^{3+}, Yang's group studied the thermal stability performance of PVC composites (Yi et al., 2011; Wen et al., 2012). All the series MgAlCe-LDH is found to impede the degradation of PVC better than pure MgAl-LDHs (Fig. 13). This could be explained that Ce^{3+} ions have a better coordination with unstable chlorine, slowing down the removal and catalysis of PVC, thus improving the thermal stability of PVC. At the same time, R.E. ions are able to scavenge HCl like MgAl-LDH. Besides, the low doping of Ce is insufficient to produce a desired synergetic effect and excessive Ce amount might damage the structure of LDHs. Experimentally, the stability of PVC composite is optimized with a ratio of Ce^{3+}: Al^{3+} of 0.075. However, PVC/MgCeAl-LDH composites are initially colored due to the fact that Mg^{2+} ions are incapable to react with labile chlorine atoms, the stability of MgCeAl-LDHs on PVC in the initial period is then not sufficient (Yi et al., 2011).

Fig. 13 (a) Effects of MgAlCe-LDH with different Ce: Al molar ratios of (a) PVC, (b) 0, (c) 0.025, (d) 0.05, (e) 0.075, and (f) 0.1 on the thermal stability of PVC composites at 180 ± 1 °C; (b) Effects of different addition of MgAlCe-LDH (Ce: Al=0.075) on the thermal stability of PVC composites at 180 ± 1 °C: (a) 2 phr, (b) 3 phr, (c) 4 phr, (d) 5 phr. Reprinted with permission from (Yi et al., 2011). Copyright (2011) John Wiley and Sons.

Since zinc element is found to delay the early coloring of PVC products, it is of significance to replace Mg^{2+} by Zn^{2+} in the host layers for further improving the initial stability of LDHs containing RE metals. Moreover, the ion radius of Zn is larger than that of Mg, which is easier for RE to dope into the layers of LDHs with the existence of metal Zn. For instance, ZnAlLa-LDHs present positive

effect on both the initial and long-term thermal stability of PVC resins. In the series, PVC composites containing 2.4 phr of LDHs have a better thermo-stabilization when the molar ratio of Zn: Al: La = 20: 8: 2 (Fig. 14). It was worth noting that the unoccupied d orbitals of La^{3+} could combine with the occupied 3d orbitals of Zn^{2+} to transform the unsuitable $ZnCl_2$ into more stable d-d complex by ionic coordination bonds, thus decreasing the deleterious catalytic effect of $ZnCl_2$. The synergistic effect between La^{2+} and Zn^{2+} ions delayed efficiently the time of "zinc burning" (Wen et al., 2012).

Fig. 14 (a) Effect of ZnAlLa-LDH with different Zn: Al: La molar ratios on the thermal stability of PVC at 180 ± 1 °C: a. PVC, b. Zn:Al:La=20:10:0, c. Zn:Al:La=20:6:4, d. Zn:Al:La=20:7:3, e. Zn:Al:La=20:8:2, f. Zn:Al:La=20:9:1; (b) Effects of different amounts of ZnAlLa-LDH (Zn:Al:La=20:8:2) on thermal stability of PVC composites at 180 ± 1 °C: a. 1.2 phr, b. 1.8 phr, c. 2.4 phr, d. 3.0 phr. Reprinted with permission from (Wen et al., 2012). Copyright (2012) Elsevier.

Some investigations focus also on the thermal stability performance of MgAl-RE-LDHs and ZnAl-RE-LDHs (RE^{3+}, one or more of Ce^{3+}, La^{3+}, Pr^{3+} or Nd^{3+}) (Zhou et al., 2011; Li et al., 2014; Yang et al., 2009 and 2010; Shen et al., 2013). Meanwhile, the quaternary RE LDHs such as MgZnAl-Ce-LDHs and MgZnAl-La-LDHs were proposed to further optimize the performance of LDHs using the interaction of the cations (Yi et al., 2014). The stability time of the rare earth metal doping LDHs could reach to over 200 min at 180 °C. In conclusion, the presence of RE^{3+} ions even in low amount is found to inhibit the initial coloring as well as to enhance efficiently the thermal stability, processability, and mechanical property of PVC products (Zhang et al., 2015a and 2015b).
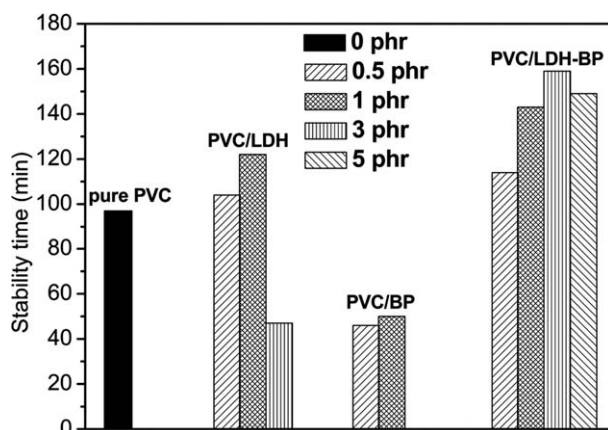
4.3 Importance of composition of interlayer guests

The interlayer guests are known to endow LDHs with predominant effect on the thermos-stabilization of polymer (Zhang et al., 2012; Yan et al., 2017). They enable to capture and react with HCl gas by ion-exchange process, thus achieving the purpose of eliminating HCl catalysis. The HCl-absorption capacity by interlayer anions plays a key role in impacting the behavior of LDHs in PVC resins. Nowadays, carbonate intercalated LDHs are the most widely used LDH thermal stabilizers, but their performance is limited owing to the single function of carbonate ions. Hence, it is a challenge to screen other anions to promote the thermal stabilization effect of LDHs (Mallakpour et al., 2017).
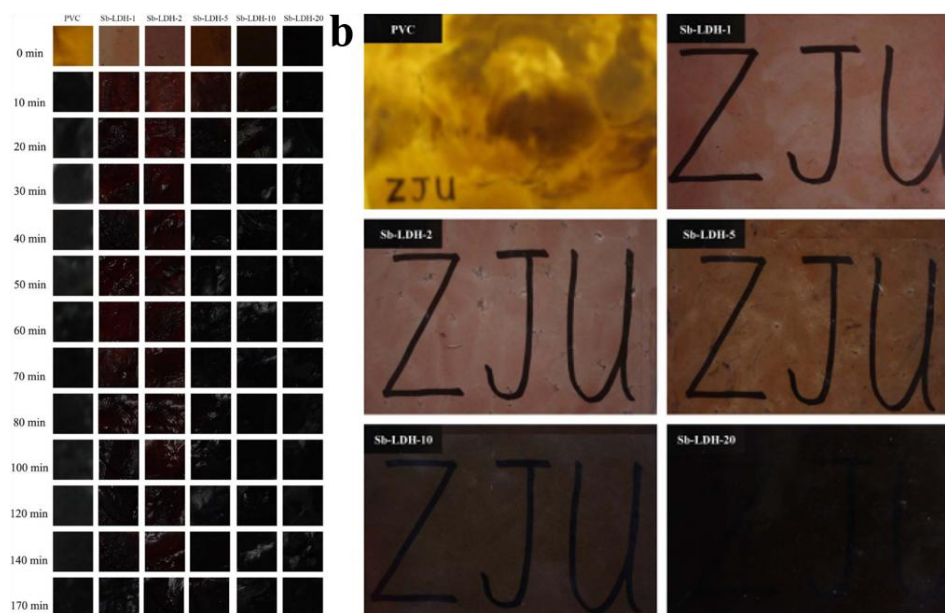
When the interlayer ions of larger size than carbonate ions are intercalated, the interlayer spacing is enlarged, reducing the hydrogen bonds between the interlayer guests and the layer hydroxyl groups. It increases the activity of hydroxyl groups to absorb HCl. For example, Zhang et al. (2012) intercalated an organic light stabilizer,2-hydroxy-4-methoxybenzophenone-5-sulfonateanion (BP⁻), as the interlayer organic guests into the MgAl-LDH galleries to obtain BP anion-intercalated LDHs (BP-LDHs) presenting both light and thermal stability. However, BP molecule possess a sulfonic acid group, which could catalyze the thermal degradation of PVC. After the intercalation, such catalytic effect of BP was restrained by the LDH structure, and the interlayer distance of LDHs increased from 0.76 to 2.33 nm after the intercalation of BP ions, which facilitated both the ingress of Cl^- into the interlayer galleries and the reaction between HCl and the layers. The order of stability time was PVC/BP-LDHs > PVC/CO$_3$-LDHs > pure PVC > PVC/BP during the Congo red test (Fig. 15), suggesting a synergistic effect between BP ions and LDHs. The results demonstrated that BP-LDHs could not only dissipate the UV light but also absorb the released HCl, which improved the resistance of PVC to both accelerated weathering and thermal degradation.

Furthermore, the interlayer anions may react with HCl or active Cl$^-$ anions, and the concomitant role of cations increases further the stability of LDHs (Mallakpour et al., 2015). For instance, organic tin acid compounds are classified as efficient PVC thermal stabilizers to react with HCl. A patent involving organic tin acid with RE-doped LDHs reports the dynamic stability and initial whiteness as a function of time, that is found superior than those of organic tin acid and CO$_3$-LDHs. This demonstrates a synergistic effect between the organic tin acid and RE-doped HT prolonging efficiently the stability time and maintains the initial whiteness of PVC products (Zhang et al., 2019). Similarly, antimony compounds were used as thermal stabilizers for dark PVC products with high efficiency. Chen (2010) and Liu et al. (2015) produced a novel thio-antimonate (SbS$_3^{3-}$) intercalated LDH as filler (Sb-LDHs) by calcination-reconstruction method. Sb-LDHs impede the increase of conjugated polyene structures in PVC and leave transparent PVC when the amount of LDHs is lower than 5 % (Fig. 16). Sb-LDHs have the potential to be a PVC stabilizer for deep-colored PVC industrial polymer since this filler is grey.
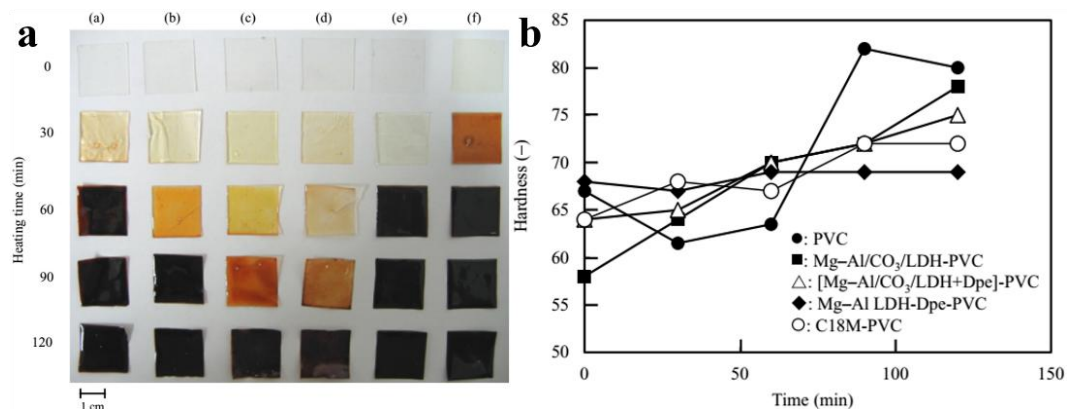

Fig. 16 (a) Photos of PVC resins and Sb-LDH/PVC composites with thickness of 2 mm. The PVC resins cover a white paper with black letters of "ZJU" drawing by a marker pen. (b) Thermal aging of PVC and Sb-LDH/PVC composites: (PVC) PVC resins without stabilizers added, (Sb-LDH-1, Sb-LDH-2, Sb-LDH-5, Sb-LDH-10, Sb-LDH-20) Sb-LDH/PVC composites. Reprinted with permission from (Liu et al., 2015). Copyright (2015) John Wiley and Sons.

Evidently, most of organic molecule's size is larger than carbonate ions, which can enlarge the interlayer distance of LDHs. In addition, organic molecules containing double bonds may be of interest to react with HCl or active Cl anions, for example. As reported in a patent, organic anions

657   having double bonds can react with conjugated double bonds by Diels-Alder reaction, stopping the

658   extend of conjugated double bonds to retard the PVC pyrolysis (Duan et al., 2005), this aspect has

659   been applied previously using maleic anhydride (Kelen et al., 1978; Garrigues et al, 1994). Another

660   Chinese patent reports the use of castor oil-based carboxylate-intercalated LDHs (Jiang et al., 2013).

661   Usually, calcium/zinc stearate LDHs are also added as it provides long-term thermal stabilizer, longer

662   than that of CO_3-LDHs. Besides, uracil derivatives are generally used as PVC thermal stabilizers to

663   inhibit the early coloring of resins because such derivatives are found to replace labile Cl atoms

664   inside PVC chains and absorb HCl gas (Xu et al., 2013). A Chinese patent reports the use of

665   barbiturate or cyanurate anions intercalated into the LDH layers with expanded basal spacing

666   increasing to stabilize PVC (Zhu et al., 2015). The stability time of PVC containing such intercalated

667   LDHs increased of about 50 min compared to that of PVC/CO_3-LDH in the Congo red test at 180 °C.

668   It is important to mention that inorganic anions may present similar properties in improving the

669   performance of PVC to the above cited organic molecules when they are intercalated into LDHs. For

670   instance, phosphate ions of larger size than CO_3^{2-} can replace the allyl chloride and react with the

671   conjugated double bonds through phosphorus-carbon coordination (Erdoğdu et al, 2008). Therefore,

672   it is of interest to study the thermal stability of phosphate ions intercalated LDHs when loaded into

673   PVC. Indeed, using CaAl-HPO_3-LDHs, Yan et al. (2017) observe that the long-term thermal stability

674   of PVC/HPO_3-LDHs is improved, as well as its early color maintained when compared with

675   PVC/CO_3-LDHs. Additionally, HPO_3-LDHs exhibit a synergetic interaction with zinc stearate to

676   maintain the long-term stability of PVC, which is explained by the fact that HPO_3^- ions react with

677    $ZnCl_2$ to generate zinc phosphate, suppressing the "zinc burning".

678

679   Fig. 17 (a) Pictures of the PVC sheets recovered after heat-resistance test at 180 °C. (a) PVC, (b) PVC/MgAl-CO_3-LDH, (c)

680   PVC/[Mg–Al-CO_3-LDH + Dpe], (d) PVC/MgAl-LDH-Dpe, (e) PVC/LiAl-LDH-Dpe, and (f) PVC/C18M; (b) Time dependence on

681   hardness of the PVC sheets recovered after the heat-resistance test at 180 °C. Reprinted with permission from (Aisawa et al., 2019).

682   Copyright (2019) Elsevier.

683   In addition, a combination of PVC stabilizer may be of interest. Aisawa et al. (2019) combined

684   molten dipentaerythritol (Dpe)with LDHs at 200-235 °C to obtain a novel effective PVC thermal

685   stabilizer. From structural analyses, the solid product (MgAl-LDH-Dpe composite) is found to form

686   disordered LDH aggregated particles covered by Dpe molecules, through hydrogen bonding. In the

687   static thermal stability test of the PVC sheets (Fig. 17a), the PVC/MgAl-LDH-Dpe composite was

688   colored slightly light-orange after 90 min and still light-brown even after 120 min, which represent

689   the higher thermal stability in the series of six PVC composites. Besides, the hardness value of

690   PVC/MgAl-LDH-Dpe composites is reported to be constant with a minimum value after 120 min,

691   (Fig. 17b). Such highly suitable performance is explained by the fact that MgAl-LDH-Dpe fillers

692   capture HCl formed by PVC degradation as well as release Dpe molecules into PVC, which then act

693   as the heat-resistant plasticizer. Also, the three-dimension network formed by PVC chains is not

694   disrupted because of the suitable particle size of LDHs. Thus, MgAl-LDH-Dpe fillers endow PVC

695   not only with a thermal stability but also - mechanical properties.

696   Different interlayer anions are ranked against the thermal stability of LDHs as a function of HCl

697   capture having the same M^{2+}: M^{3+} ratio. Van der Ven et al. (2000) measure the capacity of LDHs for

698   absorbing HCl gas and find a correlation between increasing HCl absorption and the thermal stability

699   of LDHs in the order: $SO_4^{2-} < Cl^- < OH^- \sim NO_3^- < CO_3^{2-} < C_{17}H_{35}COO^-$. Combined with the

700   above-mentioned works, it demonstrates that interlayer anions having large size as well as reacting

701   with HCl enhance the thermal stability of LDHs, and that the performance of organic guests is

702   usually better than that of inorganic anions intercalated LDHs.

703

704   **5. Conclusions**

705

706   With the improvement of specifications regarding the economy, technology and environmental

707   awareness, the development tendency for new PVC thermal stabilizers is oriented towards non-toxic,

708   environmentally friendly, economical and cheap solution. LDHs materials combine many advantages

709   as thermal stabilizers for PVC: abundant raw materials, convenient preparation, environmentally

710   friendly, excellent performance, non-toxic and low cost, all these making them expected to replace

711   the traditional PVC stabilizers but also in other industrial applications. Based on the above research

712   progress, it is well established that the chemical compositions of LDH thermal stabilizers and as well

713   as their dispersion state into polymer influence drastically the performance of PVC/LDHs

composites. At the lab-scale, LDH thermal stabilizers of excellent performance are possible to be produced by regulating the composition of layer metal cations and interlayer guest anions as well as tuning the particle size and hydrophobic modification. However, the cost of such LDH thermal stabilizers is a little higher relative to that of the traditional ones, hindering their generalization to some extent unless politic efforts are set up more restrictive health-based regulations. Therefore, it is of important to further optimize the manufacturing process of LDHs, to reduce their preparation cost as well as to continue to improve their properties. The production of multifunction LDHs additives appears as a breakthrough progress, which can challenge even better their application fields in the future.

Acknowledgements

References

Aisawa, S., Nakada, C., Hirahara, H., Takahashi, N., Narita, E., 2019. Preparation of dipentaerythritol-combined layered double hydroxide particle and its thermostabilizing effect for polyvinyl chloride. Appl. Clay. Sci. 180, 105205.

Alexandre, M., Dubois, P., 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater. Sci. Eng: R. 28, 1-63.

Bao, Y.-Z., Huang, Z.-M., Weng, Z.-X., 2006. Preparation and characterization of poly(vinyl chloride)/layered double hydroxides nanocomposite via in situ suspension polymerization. J. Appl. Polym. Sci. 102, 1471-1477.

Baum, B., Wartman, L.H., 1958. Structure and mechanism of dehydrochlorination of polyvinyl chloride, J. Polym. Sci. 28, pp. 537-546.

Cheng, H., Lei, X.-Q., 2011. Recent development in application of LDHs as heat stabilizers for PVC. Guangzhou Chemical Industry. 39, 21-23.

Chen, X.-G., Wu, D.-D., Lv, S.-S., Ying, L., Ye, Y., Cheng, J.-P., 2010. Layered double hydroxide/NaSb(OH)$_6$-poly(vinyl chloride) nanocomposites: Preparation, characterization, and thermal stability. J. Appl. Polym. Sci. 116, 1977-1984.

Chen, Y., Zhang, S.-H., Han, X.-X., Zhang, X., Yi, M.-T., Yang, S.-Y., Yu, D.-Y., Liu, W.-J., 2018. Catalytic dechlorination and charring reaction of polyvinyl chloride by CuAl layered double hydroxide. Energ. Fuel. 32, 2407-2413.

Costantino, U., Gallipoli, A., Nocchetti, M., Camino, G., Bellucci, F., Frache, A., 2005. New nanocomposites constituted of polyethylene and organically modified ZnAl-hydrotalcites. Polym. Degrad. Stab. 90, 586-590.

Dong, T.-B., Li, D.-G., Li, Y.-P., Han, W.-Y., Zhang, L.-P., Xie, G., Sunarso, J., Liu, S.-M., 2019. Design and synthesis of

751 polyol ester-based zinc metal alkoxides as a bi-functional thermal stabilizer for poly(vinyl chloride). Polym. Degrad. Stab.
752 159, 125-132.

753 Duan, X., Li, D.-Q., Lin, Y.-J., Wang, J.-R., 2005. Layered double hydroxide (LDH) with intercalated organic anions
754 having double bond, and its application as thermal stabilizer for polyvinyl chloride. CN200510117186.

755 Engwa, A.G., Ferdinand, P.U., Nwalo, N.F., Unachukwu, M.N., 2018. Mechanism and health effects of heavy metal
756 toxicity in humans. In: Karcioglu, O., Arslan, B. (Eds.), Poisoning in the Modern World. IntechOpen, pp. 77-96.

757 Evans, D.G., Duan, X., 2006. Preparation of layered double hydroxides and their applications as additives in polymers,
758 as precursors to magnetic materials and in biology and medicine. Chem. Commun. 37, 485-496.

759 Fan, G. L., Li, F., Evans, D.G., Duan, X., 2014. Catalytic applications of layered double hydroxides: recent advances and
760 perspectives. Chem. Soc. Rev. 43, 7040-7066.

761 Feng, J.-T., He, Y.-F., Liu, Y.-N., Du, Y.-Y., Li, D.-Q., 2015. Supported catalysts based on layered double hydroxides for
762 catalytic oxidation and hydrogenation: general functionality and promising application prospects. Chem. Soc. Rev. 44,
763 5291-5319.

764 Feng, Y.-J., Jiang, Y., Huang, Q., Chen, S.-T., Zhang, F.-T., Tang, P.-G., Li, D.-Q., 2014. High antioxidative performance
765 of layered double hydroxides/polypropylene composite with intercalation of low-molecular-weight phenolic antioxidant.
766 Ind. Eng. Chem. Res. 53, 2287-2292.

767 Fisch, M.H., Bacaloglu, R., 1999. Mechanism of poly(vinyl chloride) stabilisation. Plast. Rubber Compos. 28, 119–124.

768 Forano, C., Costantino, U., Prévot, V., Taviot Gueho, C., 2013. Layered double hydroxides (LDH). In: Bergaya, F.,
769 Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, pp. 745-782.

770 Gao, Y.-S., Wang, Q., Guo, Z.-H., Huang, L., Yan, X.-R., Zhang, X., He, Q.-L., Xing, Z.-P., Guo, Z.-H., 2014. Synthesis
771 of highly efficient flame retardant high-density polyethylene nanocomposites with inorgano-layered double hydroxides as
772 nanofiller using solvent mixing method. ACS Appl. Mater. Interfaces. 6, 5094−5104.

773 Gao, Y.-S., Wu, J.-W, Wang, Q., Wilkie, C.A., O'Hare, D., 2014. Flame retardant polymer/layered double hydroxide
774 nanocomposites. J. Mater. Chem. A. 2, 10996-11016.

775 Gao, Z., Lu, L., Shi, C., Qian, X.-D., 2020. The effect of OCoAl-LDH and OCoFe-LDH on the combustion behaviors of
776 polyvinyl chloride. Polym. Advan. Technol. 31, 675-685.

777 Garrigues, C., Guyot, A., Tran, V.H., 1994. Thermal dehydrochlorination and stabilization of polyvinylchloride in
778 solution: Part IX. Dialkyltin maleates: Diels-Alder reaction. Polym. Degrad. Stabil. 43, 307-311.

779 Guo, Y.-X., Wang, J., Li, D.-Q., Tang, P.-G., Leroux, F., Feng, Y.-J., 2018. Micrometer-sized
780 dihydrogenphosphate-intercalated layered double hydroxides: synthesis, selective infrared absorption properties, and
781 applications as agricultural films. Dalton Trans. 47, 3144-3154.

782

783 Gu, Z., Atherton, J.-J., Xu, Z.-P., 2015. Hierarchical layered double hydroxide nanocomposites: structure, synthesis and
784 applications. Chem. Commun. 51, 3024-3036.

785 He, J.-B, Chi, W.-J., 2017. Hydrotalcite used in polymer and preparation method therefor. WO2017080336.

786 Ishvarlal, S.J., 2018. Synthetic hydrotalcite and one pack stabilizer system for polymers. WO2018029704.

787 Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health
788 effects of some heavy metals. Interdiscip. Toxicol. 7, 60-72.

789 Jiang P.-P, Chen, H.Y., Bian, G., 2013. Method for preparing castor oil-based carboxylate-intercalated hydrotalcite for
790 PVC and composite thermal stabilizer. CN201310411252.

791 Kango, S., Kalia, S., Celli, A., Njuguna, J., Habibi, Y., Kumar, R., 2013. Surface modification of inorganic nanoparticles
792 for development of organic-inorganic nanocomposites-A review. Prog. Polym. Sci. 38, 1232-1261.

793 Kelen, T., Iván, B., Nagy, T.T., Turcsányi, b., Kennedy, J.P., 1978. Reversible crosslinking during thermal degradation of
794 PVC. PolyM. Bull. 1, 79-84.

795 Khan, A., Khan, S., Khan, M.A., Qamar, Z., Waqas, M., 2015. The uptake and bioaccumulation of heavy metals by food
796 plants, their effects on plants nutrients, and associated health risk: A review. Environ. Sci. Pollut. Res. 22,13772-13799.

797 Korkusuz, Ç., Tüzüm-Demir, A.P., 2020. Evaluation of the thermal stabilization behavior of hydrotalcite against organic
798 stabilizers for plasticized PVC films. Polym. Bull. 77, 4805-4831.

799 Kotal, M., Bhowmick, A.K., 2015. Polymer nanocomposites from modified clays: Recent advances and challenges. Prog.
800 Polym. Sci. 51, 127-187.

801 Kravchenko, J., Darrah, T.H., Miller, R.K., Lyerly, H.K., Vengosh, A., 2014. A review of the health impacts of barium
802 from natural and anthropogenic exposure. Environ. Geochem. Health 36, 797-814.

803 Kuroki, Y., Iwamoto, Y., Sawa, Y., 2016. Method for producing transparent synthetic resin molded article using
804 hydrotalcite particles. WO2016JP60546.

805 Kuroki, Y., Nakamura, T., Miyata, S., 2013. Fine hydrotalcite particles. WO2013147284.

806 Labuschagné, F.J.W.J., Molefe, D.M., Focke, W.W., Ofosu, O., 2019. Layered double hydroxide derivatives as flame
807 retardants for flexible PVC. Macromol. Symp. 384, 1800148.

808 Labuschagné, F.J.W.J., Molefe, D.M., Focke, W.W., Westhuizen, I.V.D., Wright, H.C., Royeppen, M.D., 2015. Heat
809 stabilising flexible PVC with layered double hydroxide derivatives. Polym. Degrad. Stab. 2015; 113: 46-54.

810 Lee, D.H., 2016. Hydrotalcite for PVC stabilizer and preparation of stabilizer. US20160177065.

811 Li, D.-L., Zhang, N., Yu, J., Wang, G.-R., 2014. Environment-friendly light rare earth hydrotalcites-curcumin composite
812 thermal stability additives and the preparation methods. CN201410019828.

813 Lin, Y.-J., Li, D.-Q., Evans, D.G., Duan, X., 2005. Modulating effect of Mg-Al-CO_3 layered double hydroxides on the
814 thermal stability of PVC resin. Polym. Degrad. Stab. 88, 286-293.

815 Lin, Y.-J., Li, D.-Q., Li, F., Duan, X., 2012. Method for preparation of layered hydrotalcite used as thermal stabilizer for
816 PVC in a rotary liquid membrane reactor. CN201210105842.

817 Lin, Y.-J., Wang, J.-R., Evans, D.G., Li, D.-Q., 2006. Layered and intercalated hydrotalcite-like materials as thermal
818 stabilizers in PVC resin. J. Phys. Chem. Solids. 67, 998-1001.

819 Liu, J., Chen, G.-M., Yang, J.-P., Ma, Y.-M., 2007. New facile preparation of a poly(vinyl chloride)/layered double
820 hydroxide nanocomposite via solution intercalation. Chem. Lett. 36, 1454-1455.

821 Liu, J., Chen, G.-M., Yang, J.-P., 2008. Preparation and characterization of poly(vinyl chloride)/layered double hydroxide
822 nanocomposites with enhanced thermal stability. Polymer. 49, 3923-3927.

823 Liu, J., Chen, G,-M., Yang, J.-P., Ding, L.-P., 2009. Improved thermal stability of poly(vinyl chloride) by nanoscale
824 layered double hydroxide particles grafted with toluene-2, 4-di-isocyanate. Mater. Chem. Phys. 118, 405-409.

825 Liu, S.-T., Zhang, P.-P., Yan, K.-K., Zhang, Y.-H., Ye, Y., Chen, X.-G., 2015. Sb-intercalated layered double
826 hydroxides-poly(vinyl chloride) nanocomposites: Preparation, characterization, and thermal stability. J. Appl. Polym. Sci.
827 132, 42524.

828 Li, T.-Y., Song, Y.-X., Yuan, X.-Y., Li, J.-Z., Ji, J.-F., Fu, X.-W., Zhang, Q., Guo, S.-H., 2018. Heavy metals in rice
829 (Oryza sativa L.): A probabilistic-based analysis. J. Agric. Food Chem. 66, 5683-5690.

830 Mahurpawar, M., 2015. Effects of heavy metals on human health. Int. J. Res. Grant. 3, 1-7.

831 Mallakpour, S., Dinari, M., Hatami, M., 2015. Novel nanocomposites of poly(vinyl alcohol) and Mg-Al layered double
832 hydroxide intercalated with diacid N-tetrabromophthaloyl-aspartic. J. Therm. Anal. Calorim. 120, 1293-1302.

833 Mallakpour, S., Hatami, M., 2017. Biosafe organic diacid intercalated LDH/PVC nanocomposites versus pure LDH and
834 organic diacid intercalated LDH: Synthesis, characterization and removal behaviour of Cd^{2+} from aqueous test solution.
835 Appl. Clay Sci. 149, 28-40.Ma, Y.-F., Liao, S.-L., Li, Q.-G., Guan, Q., Jia, P.-Y., Zhou, Y.-H., 2019. Physical and
836 chemical modifications of poly(vinyl chloride) materials to prevent plasticizer migration - still on the run. React. Funct.
837 Polym. 147, 104458.

838 Mishra, S., Bharagava, R.N., More, N., Yadav, A., Zainith, S., Mani, S., Chowdhary, P., 2018. Heavy metal contamination:

839 An alarming threat to environment and human health. In: Sobti, R.C., Arora, N.K., Richa, K. (Eds.), Environmental
840 Biotechnology: For Sustainable Future, Environmental Biotechnology: For Sustainable Future. Springer, pp. 103-125.

841 Mitamura, R., Nishimura, H., Tanaka, K., 2018. Vinyl chloride resin composition and its molded product. JP201888568.

842 Miyata, S., Kuroda, M., 1981. Method for inhibiting the thermal or ultraviolet degradation of thermoplastic resin and
843 thermoplastic resin composition having stability to thermal or ultraviolet degradation. US4299759.

844 Miyata, S., 1985. Progress for producing a vinyl chloride polymer or copolymer in aqueous suspension using a
845 hydrotalcite compound as suspension stabilizer. US4710551.

846 Mohammed, A.S., Kapri, A., Goel, R., 2011. Heavy metal pollution: Source, impact, and remedies. In: Khan, M.S., Zaidi,
847 A., Goel, R., Musarrat, J. (Eds.), Biomanagement of Metal-Contaminated Soils. Springer, pp, 1-28.

848 Mohod, C.V., Dhote, J., 2013. Review of heavy metals in drinking water and their effect on human health. Int. J. Innov.
849 Res. Sci. Eng. Technol. 2, 2992-2996.

850 Molefe, D.M., Labuschagné, F.J.W.J., Focke, W.W., Westhuizen, I.V.D. Ofosu, O., 2015. The effect of magnesium
851 hydroxide, hydromagnesite and layered double hydroxide on the heat stability and fire performance of plasticized
852 poly(vinyl chloride). J. Fire Sci. 33, 493-510.

853 Mori, K., Miyata, S., 2018. Microparticulate hydrotalcite and its producing method, and resin composition and
854 suspension. WO2018169019.

855 Moyo, L., Nhlapo, N., Focke, W.W., 2008. A critical assessment of the methods for intercalating anionic surfactants in
856 layered double hydroxides. J. Mater. Sci. 43, 6144-6158.

857 Nosu, T., Miyata, S., 2017. Masterbatch for polyvinyl chloride resin having improved dispersibility of hydrotalcite.
858 JP2017222174.

859 Oh, J.-M., Hwang, S.-H., Choy, J.-H., 2002. The effect of synthetic conditions on tailoring the size of hydrotalcite
860 particles. Solid State Ionics. 151, 285-291.

861 Okereafor, U., Makhatha, M., Mekuto, L., Uche-Okereafor, N., Sebola, T., Mavumengwana, Vuyo., 2020. Toxic metal
862 implications on agricultural soils, plants, animals, aquatic life and human health. Int. J. Environ. Res. Public Health 17,
863 2204.

864 Oskarsson, A., 2015. Barium. In: Nordberg, G.F., Fowler, B.A., Nordberg, M. (Eds.), 2015. Handbook on the Toxicology
865 of Metals. Elsevier, pp. 625-633.

866 Ostrakhovitch E.A., 2015. Tin. In: Nordberg, G.F., Fowler, B.A., Nordberg, M. (Eds.), 2015. Handbook on the
867 Toxicology of Metals. Elsevier, pp. 1242-1276.

868 Qiu, L., Gao, Y.-S., Lu, P., O'hare, D., Wang, Q., 2018. Synthesis and properties of polypropylene/layered double
869 hydroxide nanocomposites with different LDHs particle sizes. J. Appl. Polym. Sci. 135, 46204.

870 Qiu, X.-Q., Li, Z.-W., Li, X.-H., Zhang, Z.-J., 2018. Flame retardant coatings prepared using layer by layer assembly: A
871 review. Chem. Eng. J. 334, 108-122.

872 Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F., Kime, K.-H., 2019. Heavy metals in food crops: Health risks, fate,
873 mechanisms, and management. Environ. Int. 125, 365-385.

874 Sankhla, M.S., Kumari, M., Nandan, M., Kumar, R., 2016. Agrawal, P., Heavy metals contamination in water and their
875 hazardous effect on human health-A review. Int. J. Curr. Microbiol. App. Sci. 5, 759-766.

876 Scarpellini, D., Falconi, C., Gaudio, P., Mattoccia, A., Medaglia, P.G., Orsini, A., Pizzoferrato, R., Richetta, M., 2014.
877 Morphology of Zn/Al layered double hydroxide nanosheets grown onto aluminum thin films. Microelectron. Eng. 126,
878 129-133.

879 Schrijvers, D.L., Leroux, F., Verney, V., Patel, M.K., 2014. Ex-ante life cycle assessment of polymer nanocomposites
880 using organo-modified layered double hydroxides for potential application in agricultural films. Green Chem. 16,
881 4969-4984.

882 Shanmuganathan, K., Ellison, C.J., 2014. Layered double hydroxides: An emerging class of flame retardants in polymer

green fire retardants. In: Papaspyrides, C.D., Kiliaris, P. (Eds.), Polymer Green Flame Retardants. Elsevier, pp. 675-707.

Shao, M.-F., Zhang, R.-K., Li, Z.-H., Wei, M., Evans, D.G., Duan, X., 2015. Layered double hydroxides toward electrochemical energy storage and conversion: Design, synthesis and applications. Chem. Commun. 51, 15800-15893.

Shen, F.-L., 2017. Preparation method of nano silica core-shell particle intercalation modified hydrotalcite thermal stabilizer. CN201710596342.

Shen, W.-Q., 2013. Method for preparation of magnesium aluminum lanthanum hydrotalcite PVC composite heat stabilizer. CN201310300700.

Shimizu, S., Tsuda, T., 2017. Hydrotalcite compound, resin composition comprising the hydrotalcite compound blended therein and molded article thereof. JP201785131.

Singh, J., Kalamdhad, A.S., 2011. Effects of heavy metals on soil, plants, human health and aquatic life. Int. J. Res. Chem. Environ. 1, 15-21.

Singh, M., Singh, R.K., Singh, S.K., Mahtoa, S.K., Misra, N., 2018. In vitro biocompatibility analysis of functionalized poly(vinyl chloride)/layered double hydroxide nanocomposites. RSC Adv. 8, 40611-40620.

Slade, R.C.T., Evans, D.G., 2005. Structural aspects of layered double hydroxides. In: Duan, X., Evans, D.G. (Eds.), Layered Double Hydroxides. Springer, pp. 3-80.

Song, W.-K., Song, S.-K., Kin, H.-S., 2008. Ahn T-K. Method of manufacturing hydrotalcite. WO2008050927.

Song, Y.-F., Xie, F., Chang, W., Chen, W., 2019. Hydrotalcite PVC composite heat stabilizer with controllable diameter-thickness ratio and preparation method. CN201910408140.

Starnes, W.H., Ge, X.L., 2004. Mechanism of autocatalysis in the thermal dehydrochlorination of poly(vinyl chloride). Macromolecules. 37, 352-359.

Tang, W., Chen, Y., 2017. Present situation and development trend of PVC heat stabilizers in China. Polyvinyl Chloride. 45, 11-16.

Taviot-Guého, C., Prévot, V., Forano, C., Renaudin, G., Mousty, C., Leroux, F., 2018. Tailoring hybrid layered double hydroxides for the development of innovative applications. Adv. Funct. Mater. 28, 1703868.

Theiss, F.L., Ayoko, G.A., Frost, R.L., 2016. Synthesis of layered double hydroxides containing Mg^{2+}, Zn^{2+}, Ca^{2+} and Al^{3+} layer cations by co-precipitation methods-A review. Appl. Surf. Sci. 383, 200-213.

Titow, W.V., 1990. PVC plastics: Properties, processing, and applications. Elsevier Applied Science, pp, 3-18.

Ven, L.V.D., Gemert, M.L.M.V., Batenburg L.F., Keern, J.J., Gielgens, L.H., Koster, T.P.M., Fischer, H.R., 2000. On the action of hydrotalcite-like clay materials as stabilizers in polyvinylchloride. Appl. Clay. Sci. 17, 25-34.

Wang, D.-Y, Wilkie, C.A., 2002. Preparation of PVC-clay nanocomposites by solution blending. J. Vinyl. Addit. Techn. 8, 238-245.

Wang, G.-L., Yang, M., Li, Z.-W., Lin, K.-F., Jin, Q., Xing, C.-J., Hu, Z.-D., Wang, D., 2013. Synthesis and characterization of Zn-doped MgAl-layered double hydroxide nanoparticles as PVC heat stabilizer. J. Nanopart. Res. 15, 1882.

Wang, G.-R., Rao, D.-M., Li, K.-T., Lin, Y.-J., 2014. UV blocking by Mg-Zn-Al layered double hydroxides for the protection of asphalt road surfaces. Ind. Eng. Chem. Res. 53, 4165-4172.

Wang, X.-D., Zhang, Q., 2004. Effect of hydrotalcite on the thermal stability, mechanical properties, rheology and flame retardance of poly(vinyl chloride). Polym. Int. 53, 698-707.

Wang, X.-Z., Zhang, K., Zheng, H.-D., 2017. Method for preparing composite Mg-Al hydrotalcite thermal stabilizer applied in PVC. CN201710419642.

Wen, R.-J., Yang, Z.-H., Chen, H.-Y., Hu, Y.-W., Duan, J.-A., 2012. Zn-Al-La hydrotalcite-like compounds as heating stabilizer in PVC resin. J. Rare Earth. 30, 895-902.

Wen, X., Yang, Z.-H., Yan, J., Xie, X., 2015. Green preparation and characterization of a novel heat stabilizer for poly(vinyl chloride)-hydrocalumites. RSC Adv. 5, 32020-32026.

927 Wypych, G., 2015. Principles of thermal degradation. In: PVC degradation and stabilization (Third edition). Chem. Tec.
928 Publishing, pp. 79-165.

929 Wypych, G., 2018. Stabilization and stabilizers. In: Handbook of Material Weathering (Sixth edition). Elsevier, pp.
930 785-827.

931 Xu, J., Pan, Y.-M., Chen, Q., Wu, S.-S., 2016. Research progress of preparation and applications of layered double
932 hydroxides. China Plastics. 30, 23-29.

933 Xu, X.-P., Chen, S., Tang, W., Qu, Y.-J., Wang, X., 2013. Synthesis and application of uracil derivatives as novel thermal
934 stabilizers for rigid poly(vinyl chloride). Polym. Degrad. Stab. 981, 659-665.

935 Xu, Z.-P., Stevenson, G., Lu, C.-Q., Lu, G.-Q., 2006. Dispersion and size control of layered double hydroxide
936 nanoparticles in aqueous solutions. J. Phys. Chem. B. 110, 16923-16929.

937 Yang, H., Yang, Z.-H., 2018. The effect of sodium stearate-modified hydrocalumite on the thermal stability of
938 poly(vinyl chloride). J. Appl. Polym. Sci. 135, 45758.

939 Yang, Z.-H., Chen, H.-Y., Wen, R.-J., Yi, S., 2010. Hydrotalcite composite thermal stabilizer used for PVC.
940 CN201010298745.

941 Yang, Z.-H., Yi, S., Liu, Q.-Y., Chi, W.-W., Wang, S.-Q., Wang, S.-W., Liu, D.-R., 2009. Magnesium-aluminum-rare-
942 earth hydrotalcite complex thermal stabilizer for PVC. CN200910303613.

943 Yan, J., Yang, Z.-H., 2017. Intercalated hydrotalcite-like materials and their application as thermal stabilizers in
944 poly(vinyl chloride). J. Appl. Polym. Sci. 134, 44896.

945 Yi, S., Liu, R.-L., Fan, Y.-C., Wang, Z.-J., Zou, L., Liu, Y.-H., 2014. Rare-earth hydrotalcite composite thermal stabilizer,
946 thermal stability polyvinyl chloride and preparation method. CN201410474284.

947 Yi, S., Yang, Z.-H., Wang, S.-W., Liu, D.-R., Wang, S.-Q., Liu, Q.-Y., Chi, W.-W., 2011. Effects of MgAlCe-CO$_3$ layered
948 double hydroxides on the thermal stability of PVC resin. J. Appl. Polym. Sci. 119, 2620-2626.

949 Yu, J., Sun, L., Ma, C., Qiao, Y., Yao., H., 2016. Thermal degradation of PVC: A review. Waste Manage. 48, 300-314.

950 Yu, J., Wang, Q., O'Hare, D., Sun, L.-Y., 2017. Preparation of two dimensional layered double hydroxide nanosheets and
951 their applications. Chem. Soc. Rev. 46, 5950-5974.

952 Zahra, N., Kalim, I., Mahmood, M., Naeem, N., 2017. Perilous effects of heavy metals contamination on human health.
953 Pak. J. Anal. Environ. Chem. 18, 1-17.

954 Zammarano, M., Franceschi, M., Bellayera, S., Gilmana, J.W., Meriani, S., 2005. Preparation and flame resistance
955 properties of revolutionary self-extinguishing epoxy nanocomposites based on layered double hydroxides. Polymer. 46,
956 9314-9328.

957 Zhang, D.-F., Yao, S., Li, S., Wang, J., You, J.-W., 2017. A novel La-containing additive for the long-term thermal
958 stabilization of poly(vinyl chloride). Polym. Degrad. Stab. 144, 187-194.

959 Zhang, H.-M., Zhang, S.-H., Stewart, P., Zhu, C.-H., Liu, W.-J., Hexemer, A., Schaible, E., Wang, C., 2016. Thermal
960 stability and thermal aging of poly(vinyl chloride)/MgAl layered double hydroxides composites. Chinese J. Polym. Sci.
961 34, 542-551.

962 Zhang, N., 2015a. Composite heat stabilizer containing rare earth hydrotalcite for PVC and preparation method.
963 CN201510047764.

964 Zhang, N., Li, X.-M., Zhang, Q., Yang, X.-C., Li, D.-L., 2015b. Magnesium-light rare earth hydrotalcite composite heat
965 stabilizer for PVC with improved processability, and preparation method. CN201510047520.

966 Zhang, N., Li, X.-M., 2019. Organic stannic acid intercalated calcium/zinc-aluminum rare earth hydrotalcite composite
967 heat stabilizer for rigid PVC and preparation method. CN201910676040.

968 Zhang, Q., Guo, Y.-X., Marek, A.A., Verney, V., Leroux, F., Tang, P.-G., Li, D.-Q., Feng, Y.-J., 2019. Design, fabrication
969 and anti-aging behavior of a multifunctional inorganic-organic hybrid stabilizer derived from co-intercalated layered
970 double hydroxides for polypropylene. Inorg. Chem. Front. 6, 2539-2549.

971   Zhang, Q., Leroux, F., Tang, P.-G., Li, D.-Q., Feng, Y.-J., 2018. Low molecular weight hindered amine light stabilizers

972   (HALS) intercalated MgAl-Layered double hydroxides: Preparation and anti-aging performance in polypropylene

973   nanocomposites. Polym. Degrad. Stab. 154, 55-61.

974   Zhang, S.-H., 2018. Hydrothermal synthesis method for increasing initial whiteness of hydrotalcite. CN201810785546.

975   Zhang, W., Dong, D.-D., Wei, Z., Ma, Y.-Q., 2014. Synthesis of lanthanum ricinoleate and its effect on thermal stability

976   and mechanical properties in PVC. J. Rare. Earth. 32, 1089-1094.

977   Zhang, X.-F., Zhao, T.-B., Pi, H., Guo, S.-Y., 2012. Preparation of intercalated Mg-Al layered double hydroxides and its

978   application in PVC thermal stability. J. Appl. Polym. Sci. 124, 5180-5186.

979   Zhao, Y., Li, F., Zhang, R., Evans, D.G., Duan, X., 2002. Preparation of layered double hydroxide nanomaterials with a

980   uniform crystallite size using a new method involving separate nucleation and aging steps. Chem. Mater. 14, 4286-4291.

981   Zhou, J.-L., Zhu, J., Huang, H.-Z., Sun, Y.-L., 2011. Preparation and application of Zn-Al-rare earth hydrotalcite

982   composite heat stabilizer for PVC. CN201110001912.

983   Zhou, X., Yuan, H.-K., Jiang, S.-W., 2017a. A type of modified hydrotalcite for PVC thermal stabilizer and its preparation

984   method. CN201710129104.

985   Zhou, X., Yuan, H.-K., Jiang, S.-W., 2018. Eco-friendly method for preparing modified hydrotalcite as PVC heat

986   stabilizer. CN201810245736.

987   Zhou, X., Yuan, H.-K., Zhang, C., 2017b. A type of modified magnesium zinc-aluminum hydrotalcite for PVC thermal

988   stabilizer and its preparation method. CN201710129132.

989   Zhu, H., Wang, W.-S., Liu, T.-X., 2011. Effects of copper-containing layered double hydroxide on thermal and smoke

990   behavior of poly(vinyl chloride). J. Appl. Polym. Sci. 122, 273-281.

991   Zhu, L.-Z., Chen, M., Shentu, B.Q., Ye, Z.-Q., Wu, Y.-J., Liu, Y.-Y., Weng, Z.-X., 2015. Preparation method of anion

992   intercalation modified hydrotalcite for PVC hard products. CN201510460670.