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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

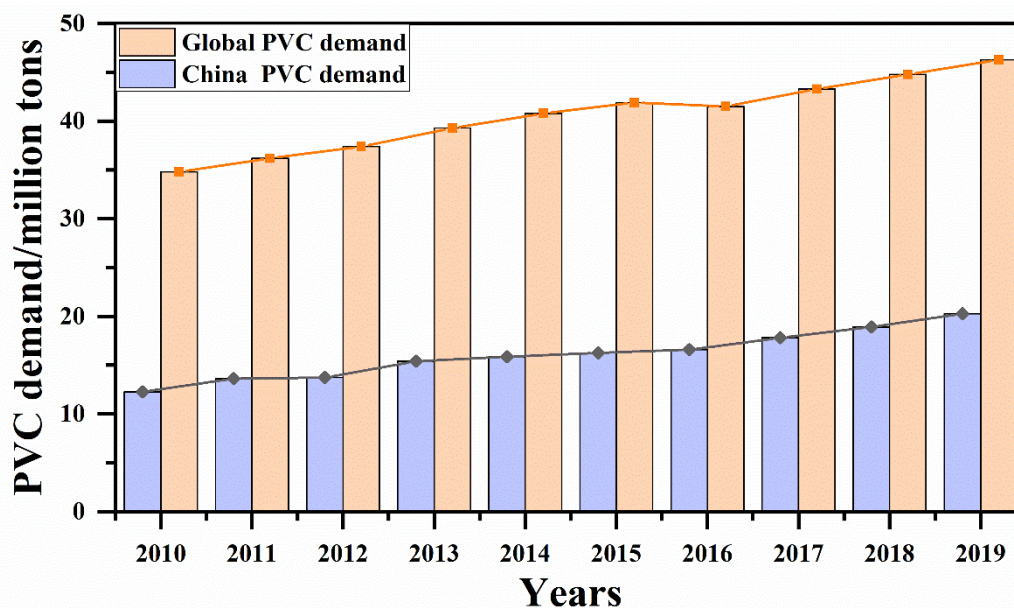
Abstract: Poly(vinyl chloride) (PVC), an important thermoplastic polymer widely-used in various fields, requires the use of thermal stabilizers to enhance its thermal stability during polymer processing and practical applications because of the poor thermal stability. Layered double hydroxides (LDHs), 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

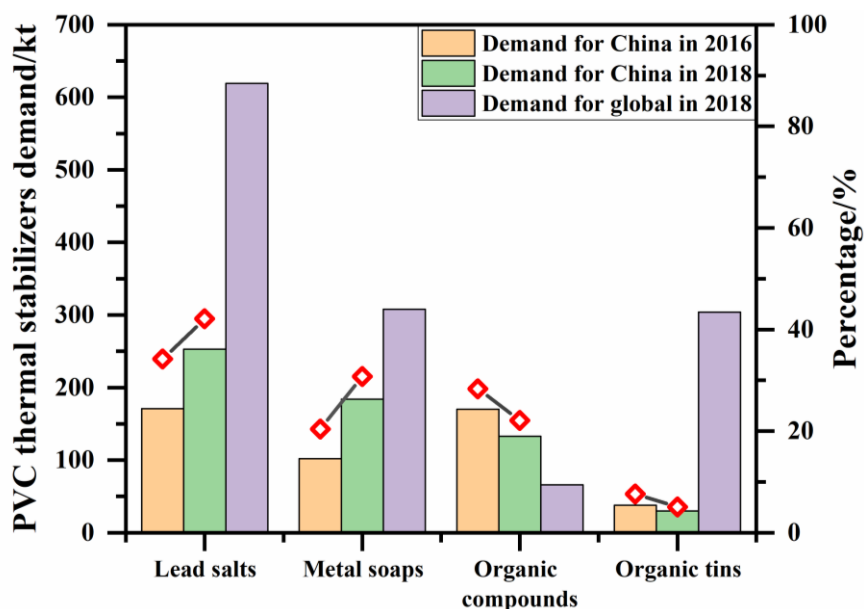
32 industries (Titow, 1990; Ma et al., 2019). According to market research institute IHS Markit
33 (<https://ihsmarkit.com/>), overall global demands for PVC grew from 2010 to 2019 and reached 46.3
34 million tons in 2019 with a compound annual growth rate (CAGR) of 2.9 %. North-East Asia
35 provides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



39
40 Fig. 1 global and Chinese PVC demand and relative variation trends from 2010 to 2019.

41 However, PVC has poor thermal stability and is easy degraded to produce hydrogen chloride
42 (HCl) gas during processing and its application due to the unstable structure (e.g., allyl chloride,
43 tertiary chloride, and head-to-head structure) in its polymer chains. Simultaneously, the formation of
44 carbon-carbon double bonds can active the adjacent carbon to further generate more double bonds as
45 well as HCl. In turn, the HCl gas accelerates catalytically the degradation process of PVC, causing
46 the formation of polyene sequences of π -conjugated double bonds. This process is called the zipper
47 autocatalytic dehydrochlorination, which leads to the discoloration and deterioration of mechanical
48 properties of PVC products as a function of time. Particularly, the thermoforming temperature
49 (160-210 °C) of PVC products is much higher than their thermal degradation temperature (about
50 100 °C), which severely affects the processing and practical application of PVC products (Wypych et
51 al., 2015). Therefore, it is necessary to use special thermal stabilizers to restrain thermal damage due
52 to the high temperatures occurring during the polymer process (Fisch et al., 1999). Indeed, PVC
53 thermal stabilization has been addressed since the early 70's when PVC was still the second

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



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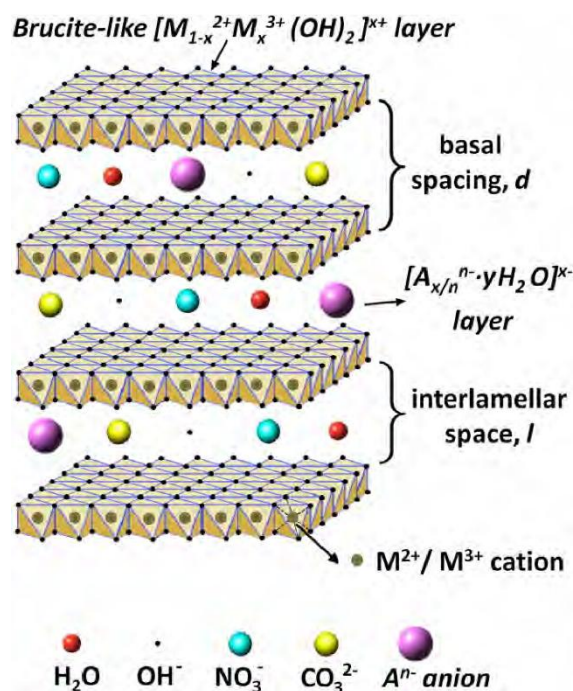
Fig. 2 The demand and the relative percentage for lead salts, metal soaps, organic compounds and organic tins in China (2016 and 2018) and global (2018) (<https://www.chyxx.com/>)

61 According to the statistics by Research and Markets (<https://www.researchandmarkets.com/>),
 62 the global thermal stabilizer consumption was 1296 kilotons in 2018, with a high proportion of PVC
 63 products containing lead salts, metal soaps, organic compounds and organic tins as follows 47.74 %,
 64 23.80 %, 5.03 %, and 23.43 %, respectively (Fig. 2). With about 46 % globally produced in 2018,
 65 China has consumed about 600 kilotons PVC thermal stabilizers. With the expansion of application
 66 range of PVC products, the demand for global PVC thermal stabilizers is expected to increase
 67 rapidly at a CAGR of around 6 % in a near future. The awareness of the importance for green
 68 additives is growing, triggered by the growth of PVC market, leading to a higher demand for
 69 low-cost and environment-friendly thermal stabilizers. Due to the high toxicity of lead, the RoHS
 70 directive issued in 2003 and the REACH regulations implemented in 2007 by the European Union
 71 (EU) control strictly the use of lead salts, and completely banned lead in the EU in late 2015. There
 72 is no doubt that the safety of plastic products is of importance because they are closely related to the
 73 daily life of people and to their health. However, a large number of lead salts are still produced and
 74 used in parts of Asia-Pacific and Africa regions due to the limit of technology and industrial
 75 innovation. To date, the development of relative eco-friendly thermal stabilizers such as calcium/zinc

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

86 In 1981, the patent reported by Kyowa Chemical Industries of Japan firstly indicated that
87 two-dimensional (2D) layered double hydroxides (LDHs) could significantly improve the
88 performance of PVC composites (Forano et al., 2013; Miyata et al., 1981). Indeed, LDH thermal
89 stabilizers, as a novel eco-friendly PVC thermal stabilizer, have received considerable attention and
90 produced in a large-scale with convenient preparation, yielding to excellent performance, low cost,
91 and non-toxic PVC filler (Xu et al., 2016; Cheng et al., 2011). LDH materials are comprised by a
92 positively charged brucite-like layer in the host layers, and negatively intercalated guest anions in the
93 interlayer region as well as water molecules (Evans et al., 2006). Generally, the chemical formula of
94 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
95 trivalent metal cations in the host layers; x is the surface charge and the value of that is determined
96 by the molar ratio M^{3+} : ($M^{2+}+M^{3+}$); A^{n-} represents interlayer inorganic or organic guest anions of
97 charge n; z is the number of water molecules in the gallery (Fan et al., 2014). The typical structure of
98 LDHs is similar to that of brucite ($Mg(OH)_2$) (Scarpellini et al., 2014) (Fig. 3). Up to now, LDHs
99 have been designed by adjusting their chemical compositions, the exchangeable guest anions, as well
100 as by tuning their particle size and controlling their surface properties to address suitable
101 functionality (Taviot-Guého et al., 2018; Feng et al., 2015; Slade et al., 2005; Shao et al., 2015).
102 Such functionalities are of great interest for application, as exemplified by the domain of polymer
103 composites (Gu et al., 2015; Schrijvers et al., 2014), heat retention additives (Guo et al., 2018),
104 ultraviolet absorbers (Wang et al., 2014), flame retardants (Qiu et al., 2018; Gao et al., 2014;
105 Shanmuganathan et al., 2014; Costantino et al., 2005; Zammarano et al., 2005), antioxidant (Feng et
106 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.

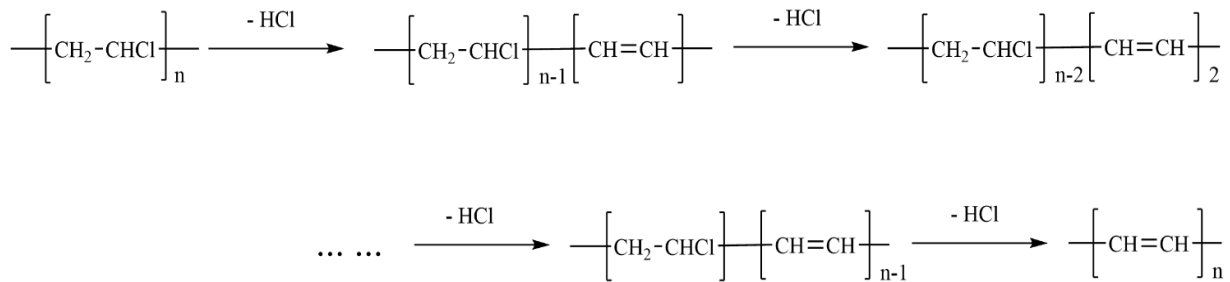
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116 2. Thermal stabilization mechanism

117

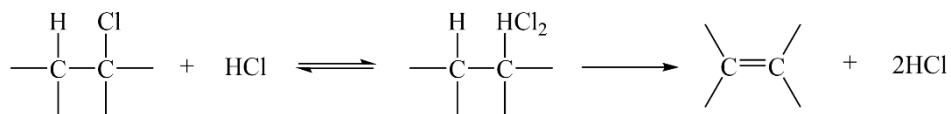
118 PVC resins suffer severely from thermal degradation under temperatures higher than 100 °C and
 119 from UV radiation due to the presence of labile chloride ions in the polymer chains. The thermal
 120 dehydrochlorination process of PVC is initiated at defect sites and starts to generate C-C double
 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



129

130 (2) The process of HCl catalytic reaction



131

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 SO₄²⁻ and NO₃⁻ (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.

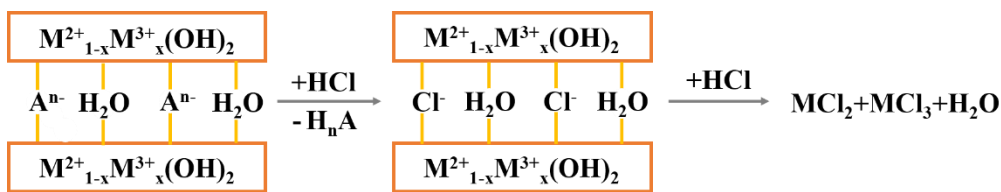


Fig. 4 Schematic illustration for the reaction between the LDHs and HCl gas.

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 its 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

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

190

191 **3.1 Lead**

192

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

206

207 **3.2 Cadmium**

208

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

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

220

221 **3.3 Tin**

222

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

233

234 **3.4 Zinc**

235

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

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

247

248 **3.5 Barium**

249

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

258

259 **4. The interest of LDH layers**

260

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

265

266 **4.1 Importance of layers dispersion and distribution**

267

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

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

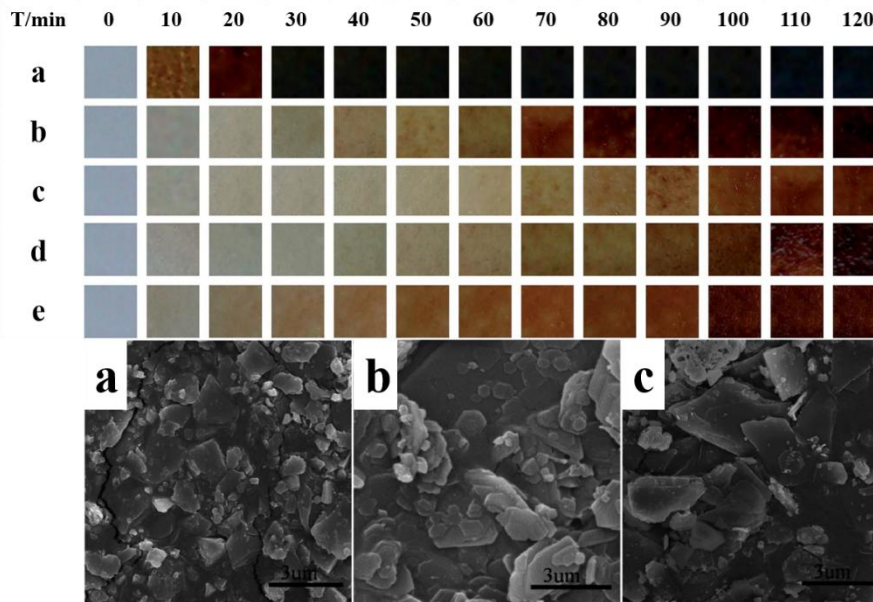
282 283 4.1.1 Control of particle size and particle size distribution

284
285 Previous studies report that LDH particles with small size and narrower size distribution are
286 well dispersed in PVC/LDHs composites. Chemical and/or technological processes are applied to
287 control size and size distribution as exemplified with separate nucleation and aging steps (SNAS)
288 method, hydrothermal synthesis method and ammonia-releasing method). It is possible to adjust the
289 reaction conditions (e.g., reaction time, temperature and concentration, etc.) to control precisely the
290 particle size in the range from nanometer to micron with the narrow size distribution, thus
291 broadening the possible application of LDHs as filler for polymer (Theiss et al., 2016; Zhao et al.,
292 2002; Xu et al., 2006; Oh et al., 2002; Qiu et al., 2018).

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

300 Based on the above work, the research group at BUCT fabricated a series of MgAl- CO_3 -LDH of
301 size from 202 to 334 nm using $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and light magnesium carbonate (LMC) as
302 starting materials, and studied the influence of different-sized LDH particles on thermal stability
303 property of LDHs/PVC composites. The order of induction time of HCl evolution for LDHs/PVC
304 composites is reported in Fig. 6. It shows as a function of the particle size a small induction time for
305 tiny particles that is optimized for a particle size of 220 nm then it is found to decrease again (Fig. 5).

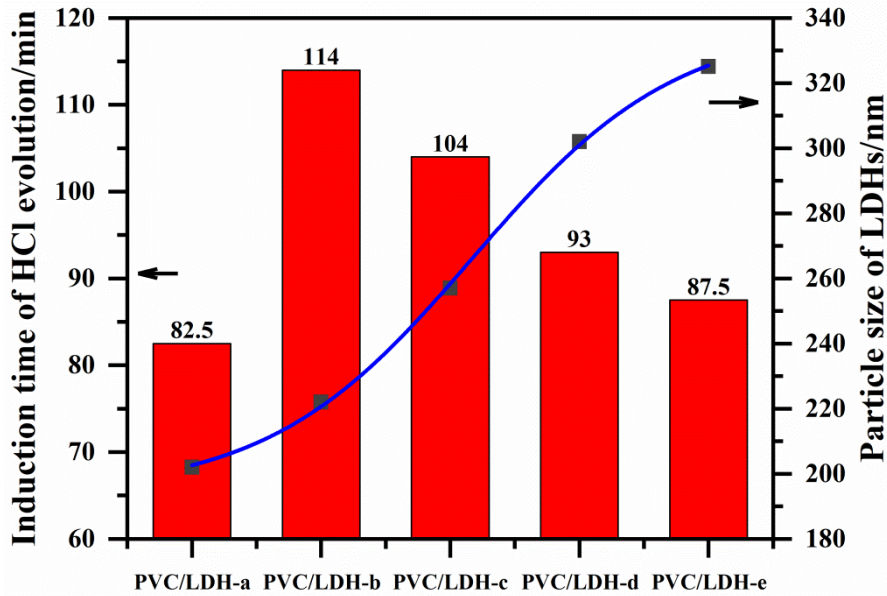
306 It is probably due to the fact that the sample of very small particle size (LDH-a) is inclined to
 307 agglomerate, affecting the dispersion of particles into PVC, while the LDH filler of larger size than
 308 220 nm (LDH-b) exhibits lower compatibility with PVC. This work further demonstrates that the
 309 particle size of stabilizers plays a key role in improving the thermal stability of PVC by influencing
 310 the dispersion state of LDH platelets in PVC.



311
 312 Fig. 5 (a-c) SEM images of hydrocalumites prepared with different reaction time and crystallization times; (d) Effect of
 313 hydrocalumites prepared with different reaction time and crystallization time on the stability of PVC at 195 ± 1 °C. Reprinted with
 314 permission from (Wen et al., 2015). Copyright (2015) The Royal Society of Chemistry.

315 Besides, different synthesis methods are available to tune the particle size of LDH platelets. A
 316 Chinese patent reports a method for preparing LDHs in a rotary liquid membrane reactor, this is
 317 found to improve the nucleation rate and reduce the crystal growth rate. The LDH particle size are
 318 small ranging from 10 to 150 nm with a narrow particle size distribution range (20-50 nm), this
 319 should be beneficial to disperse LDH particles into PVC (Lin et al., 2012). The LDHs prepared by
 320 the above method supplies a good initial stability and increases the initial whiteness of PVC products
 321 (Zhang et al., 2018). Later, another two Japanese patents report that the LDH particles with small
 322 particle size improve both the thermal stability and transparency of PVC resins. Stabilized as a
 323 suspension, small particles do not aggregate, leading to their efficient dispersion (Kurogi et al., 2013;
 324 Nosu et al., 2017). For the aggregation of LDHs when using smaller particles occurring during both
 325 drying process and long-term storage in suspension, it was proposed to improve the dispersion state
 326 of LDHs by reducing the lattice distortion of (003) direction to 3×10^{-3} or less and adjusting the
 327 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.

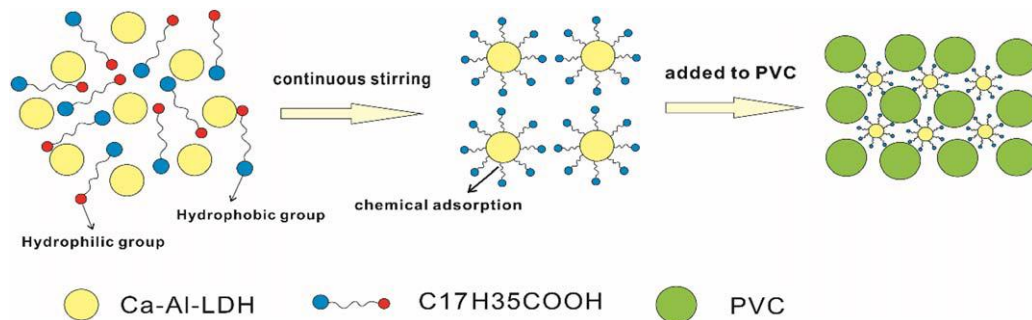
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336 4.1.2 Surface modification of LDHs

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 ($\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$, DS^-) and stearate ($\text{C}_{17}\text{H}_{37}\text{COO}^-$, 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).

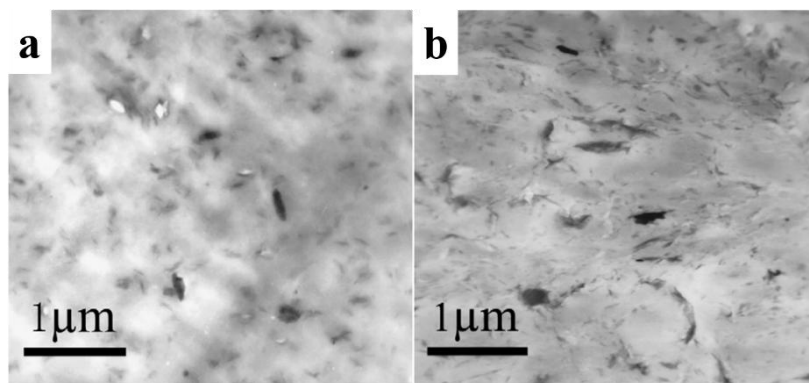


368
 369 Fig. 7 Schematic illustration for the modification of CaAl-LDHs by sodium stearate. Reprinted with permission from (Yang et al., 2018).
 370 Copyright (2018) John Wiley and Sons.

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 $\text{CO}(\text{NH}_2)_2$ 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- $\text{CO}(\text{NH}_2)_2$ -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.

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

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

426

427 **4.2 Importance of metal composition in LDH layers**

428

429 The surface of LDH layers is alkaline, consisting of hydroxy groups, and LDH thermal
430 stabilizers could absorb effectively and neutralize HCl gas generated from the degradation, acting as
431 a buffer to improve the thermal stability of PVC. The properties of LDH layers are influenced by the
432 metal compositions. Therefore, the possibility to tune the metal composition of LDHs can further
433 enhance the HCl absorption ability or promote the coordination with active Cl⁻ anions. This is

434 exemplified by selecting metal cations and tailoring the layer and interlayer compositions to optimize
 435 the stability of LDHs (Yu et al., 2017; Labuschagné et al., 2019). MgAl-LDHs is the most commonly
 436 used LDH thermal stabilizer, and there are two main routes to further raise the performance of LDHs:
 437 (1) The introduction of metal cations with stronger electronegativity such as Zn^{2+} , Cu^{2+} enables to
 438 decrease the interaction between hydroxyl group and host layers as well as promote the reaction
 439 between hydroxyl group and HCl gas; (2) Doping rare earth metals (e.g., Ce^{3+} , La^{3+}) into the LDH
 440 layers can coordinate with active Cl atoms in polymer chains by electrostatic attraction.

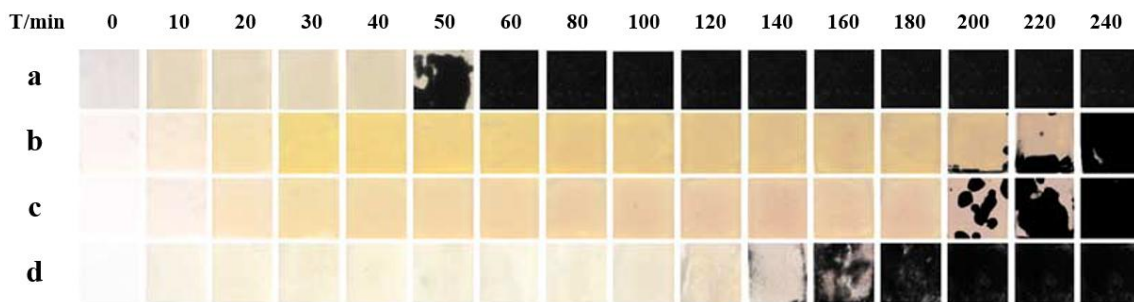
441

442 4.2.1 Incorporation of metal elements with higher electronegativity into LDH layers

443

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

450



451 Fig. 9 Thermal stability of (a) PVC reference and samples of PVC containing (b) MgAl-CO₃-LDH, (c) MgZnAl-CO₃-LDH and (d)
 452 MgZnAl-maleate-LDH. Reprinted with permission from (Lin et al., 2006). Copyright (2006) Elsevier.

453 The cation substitution of metal elements of higher electronegativity than Mg^{2+} decreases the
 454 electronegativity of the layers, thus weakening the interaction between the host layers and the
 455 hydroxyl groups with a reactivity improved. Meanwhile, metal cations of larger ion radius than Mg^{2+}
 456 will decrease the M-O bond strength with the longer bond distance, thus weakening the interaction
 457 between hydroxyl groups and the interlayer ions. It is presumed that the substitution of metal
 458 elements with the above characteristics can increase the HCl absorption capacity of LDHs, thus
 459 optimizing the thermal stability of PVC. For instance, the electronegativity of zinc is 1.65, higher
 460 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.

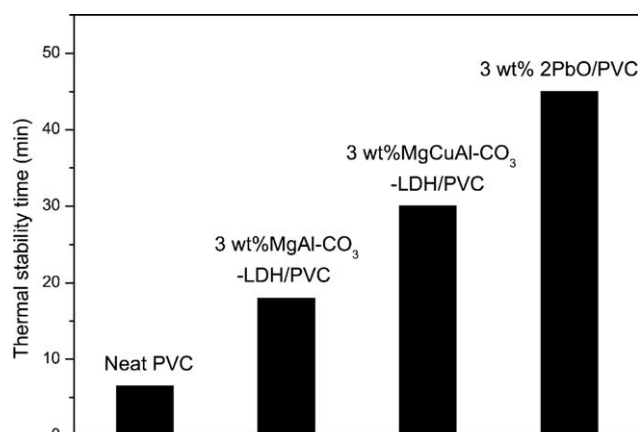
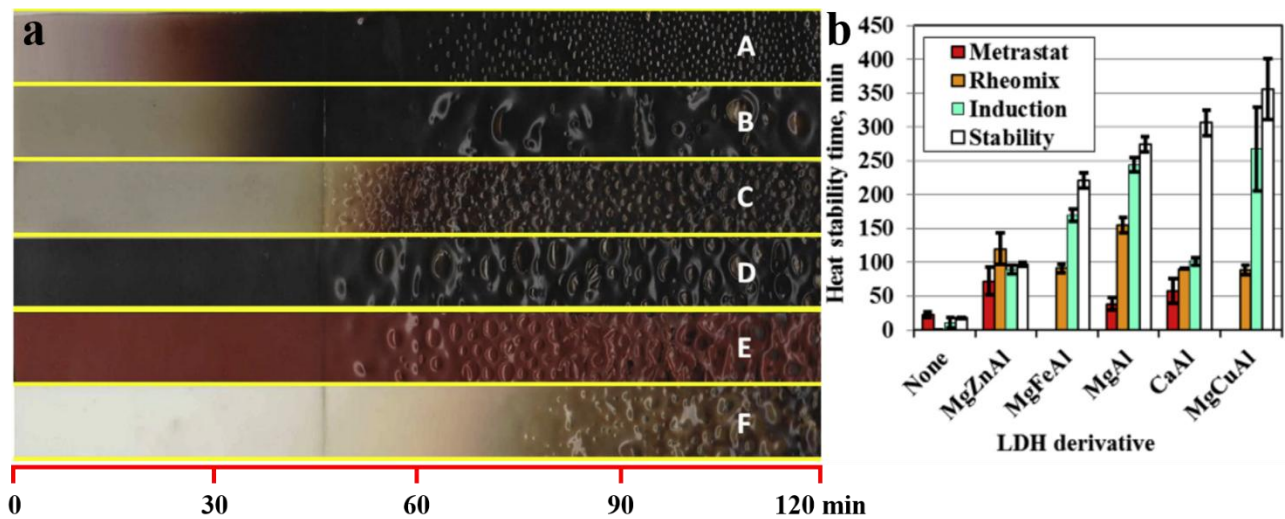


Fig. 10 Thermal stability time of neat PVC and its composites containing lead salts, MgAl-CO₃-LDH and MgCuAl-CO₃-LDH measured by Congo red tests. Reprinted with permission from (Zhu et al., 2011). Copyright (2011) John Wiley and Sons.

A recent example of such cation substitution in LDH layers was reported by Labuschagné and co-workers (2015), by substitution between Zn²⁺, Fe²⁺, Ca²⁺ and Cu²⁺ cations to produce MgMAI-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 Fe³⁺ and Cu²⁺ 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 MgCl₂, ZnCl₂, CaCl₂, and AlCl₃, respectively (Ishvarlal et al., 2018). Zinc element presents a positive influence on the initial period to stabilize PVC but also a negative effect

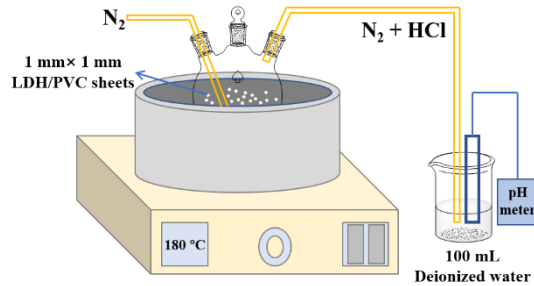
516 on the long period because the $ZnCl_2$ product promotes PVC decomposition. The preparation of
 517 quaternary LDHs can utilize the advantage of Zn element and avoid the drawback of $ZnCl_2$ due to
 518 the synergetic effect between four metal elements. To sum up this part, the cation substitution 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

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



542

543

Fig. 12 Schematic diagram of dehydrochlorination test equipment.

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

556

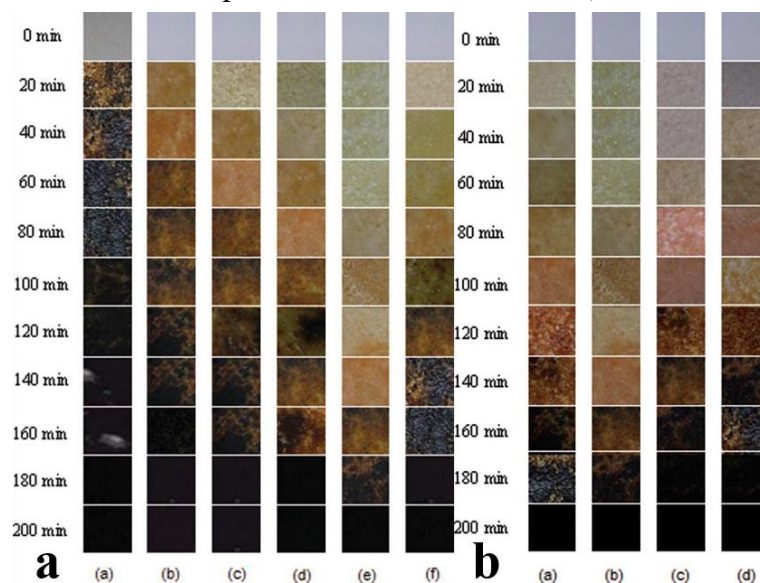
557 4.2.2 Incorporation of rare earth elements into LDH layers

558

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

566 down the degradation rate (Zhang et al., 2017; Zhang et al., 2014). Thus, an enticing approach is to
 567 combine LDHs and R.E. elements to further optimize the thermal stability of LDHs in PVC by
 568 doping rare earth cations (RE^{3+}) into LDH host layers.

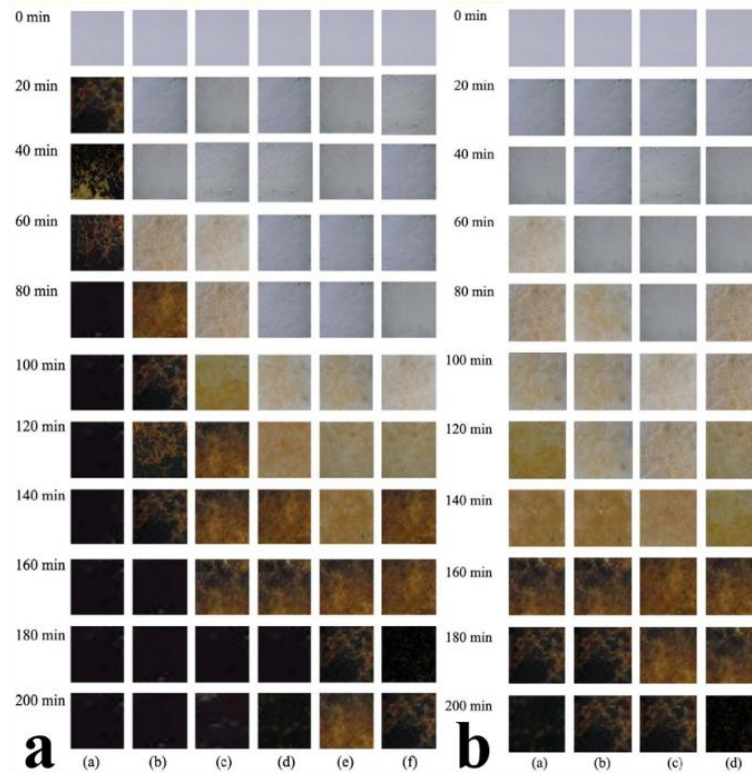
569 Using MgAlCe-LDHs and ZnAlLa-LDHs as filler with varying molar ratios of $RE^{3+}: Al^{3+}$,
 570 Yang's group studied the thermal stability performance of PVC composites (Yi et al., 2011; Wen et
 571 al., 2012). All the series MgAlCe-LDH is found to impede the degradation of PVC better than pure
 572 MgAl-LDHs (Fig. 13). This could be explained that Ce^{3+} ions have a better coordination with
 573 unstable chlorine, slowing down the removal and catalysis of PVC, thus improving the thermal
 574 stability of PVC. At the same time, R.E. ions are able to scavenge HCl like MgAl-LDH. Besides, the
 575 low doping of Ce is insufficient to produce a desired synergetic effect and excessive Ce amount
 576 might damage the structure of LDHs. Experimentally, the stability of PVC composite is optimized
 577 with a ratio of $Ce^{3+}: Al^{3+}$ of 0.075. However, PVC/MgCeAl-LDH composites are initially colored
 578 due to the fact that Mg^{2+} ions are incapable to react with labile chlorine atoms, the stability of
 579 MgCeAl-LDHs on PVC in the initial period is then not sufficient (Yi et al., 2011).



580
 581 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
 582 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
 583 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).
 584 Copyright (2011) John Wiley and Sons.

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

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



595
 596 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.
 597 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
 598 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.
 599

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600 Some investigations focus also on the thermal stability performance of MgAl-RE-LDHs and
 601 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;
 602 Yang et al., 2009 and 2010; Shen et al., 2013). Meanwhile, the quaternary RE LDHs such as
 603 MgZnAl-Ce-LDHs and MgZnAl-La-LDHs were proposed to further optimize the performance of
 604 LDHs using the interaction of the cations (Yi et al., 2014). The stability time of the rare earth metal
 605 doping LDHs could reach to over 200 min at 180 °C. In conclusion, the presence of RE^{3+} ions even
 606 in low amount is found to inhibit the initial coloring as well as to enhance efficiently the thermal
 607 stability, processability, and mechanical property of PVC products (Zhang et al., 2015a and 2015b).

608

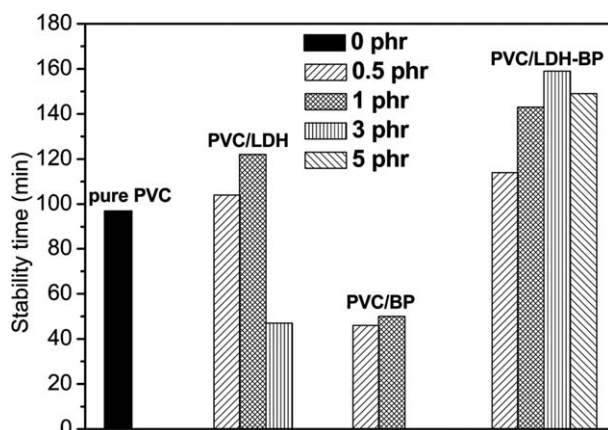
609 4.3 Importance of composition of interlayer guests

610

611 The interlayer guests are known to endow LDHs with predominant effect on the
612 thermos-stabilization of polymer (Zhang et al., 2012; Yan et al., 2017). They enable to capture and
613 react with HCl gas by ion-exchange process, thus achieving the purpose of eliminating HCl catalysis.
614 The HCl-absorption capacity by interlayer anions plays a key role in impacting the behavior of LDHs
615 in PVC resins. Nowadays, carbonate intercalated LDHs are the most widely used LDH thermal
616 stabilizers, but their performance is limited owing to the single function of carbonate ions. Hence, it
617 is a challenge to screen other anions to promote the thermal stabilization effect of LDHs (Mallakpour
618 et al., 2017).

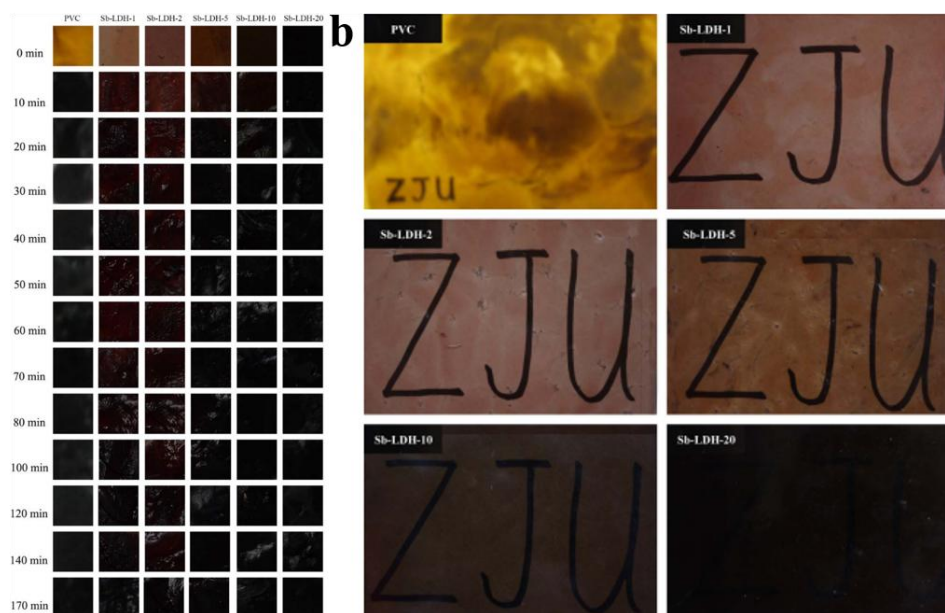
619 When the interlayer ions of larger size than carbonate ions are intercalated, the interlayer
620 spacing is enlarged, reducing the hydrogen bonds between the interlayer guests and the layer
621 hydroxyl groups. It increases the activity of hydroxyl groups to absorb HCl. For example, Zhang et al.
622 (2012) intercalated an organic light stabilizer, 2-hydroxy-4-methoxybenzophenone-5-sulfonate anion
623 (BP⁻), as the interlayer organic guests into the MgAl-LDH galleries to obtain BP anion-intercalated
624 LDHs (BP-LDHs) presenting both light and thermal stability. However, BP molecule possess a
625 sulfonic acid group, which could catalyze the thermal degradation of PVC. After the intercalation,
626 such catalytic effect of BP was restrained by the LDH structure, and the interlayer distance of LDHs
627 increased from 0.76 to 2.33 nm after the intercalation of BP ions, which facilitated both the ingress of
628 Cl⁻ into the interlayer galleries and the reaction between HCl and the layers. The order of stability
629 time was PVC/BP-LDHs > PVC/CO₃-LDHs > pure PVC > PVC/BP during the Congo red test (Fig.
630 15), suggesting a synergistic effect between BP ions and LDHs. The results demonstrated that
631 BP-LDHs could not only dissipate the UV light but also absorb the released HCl, which improved
632 the resistance of PVC to both accelerated weathering and thermal degradation.

633



634 Fig. 15 Thermal stability time of PVC, CO₃-LDH/PVC, BP/PVC and BP-LDH/PVC measured by Congo red test. Reprinted with
635 permission from (Zhang et al., 2012). Copyright (2012) John Wiley and Sons.

636 Furthermore, the interlayer anions may react with HCl or active Cl⁻ anions, and the concomitant
637 role of cations increases further the stability of LDHs (Mallakpour et al., 2015). For instance, organic
638 tin acid compounds are classified as efficient PVC thermal stabilizers to react with HCl. A patent
639 involving organic tin acid with RE-doped LDHs reports the dynamic stability and initial whiteness as
640 a function of time, that is found superior than those of organic tin acid and CO₃-LDHs. This
641 demonstrates a synergistic effect between the organic tin acid and RE-doped HT prolonging
642 efficiently the stability time and maintains the initial whiteness of PVC products (Zhang et al., 2019).
643 Similarly, antimony compounds were used as thermal stabilizers for dark PVC products with high
644 efficiency. Chen (2010) and Liu et al. (2015) produced a novel thio-antimonate (SbS₃³⁻) intercalated
645 LDH as filler (Sb-LDHs) by calcination-reconstruction method. Sb-LDHs impede the increase of
646 conjugated polyene structures in PVC and leave transparent PVC when the amount of LDHs is lower
647 than 5 % (Fig. 16). Sb-LDHs have the potential to be a PVC stabilizer for deep-colored PVC
648 industrial polymer since this filler is grey.

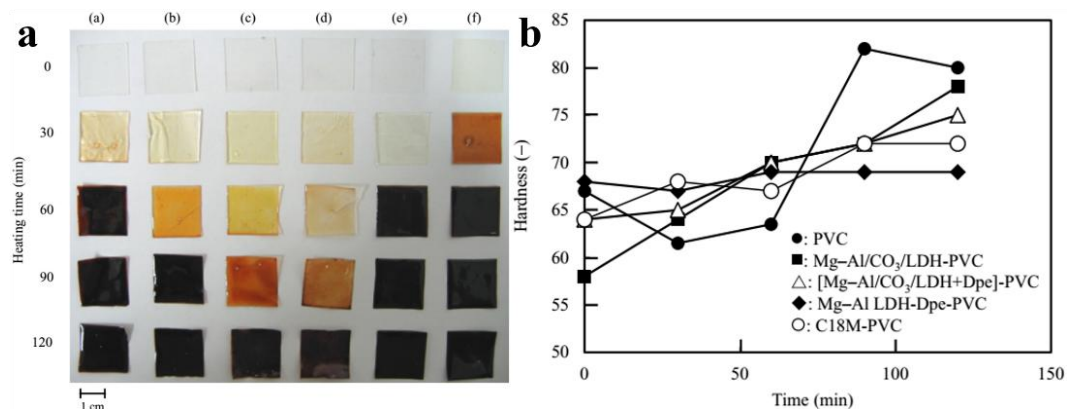


649
650 Fig. 16 (a) Photos of PVC resins and Sb-LDH/PVC composites with thickness of 2 mm. The PVC resins cover a white paper with
651 black letters of “ZJU” drawing by a marker pen. (b) Thermal aging of PVC and Sb-LDH/PVC composites: (PVC) PVC resins without
652 stabilizers added, (Sb-LDH-1, Sb-LDH-2, Sb-LDH-5, Sb-LDH-10, Sb-LDH-20) Sb-LDH/PVC composites. Reprinted with permission
653 from (Liu et al., 2015). Copyright (2015) John Wiley and Sons.

654 Evidently, most of organic molecule’s size is larger than carbonate ions, which can enlarge the
655 interlayer distance of LDHs. In addition, organic molecules containing double bonds may be of
656 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 CO₃-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/CO₃-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 CO₃²⁻ can replace the allyl chloride and react with the
 671 conjugated double bonds through phosphorus-carbon coordination (Erdođdu 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-HPO₃-LDHs, Yan et al. (2017) observe that the long-term thermal stability
 674 of PVC/HPO₃-LDHs is improved, as well as its early color maintained when compared with
 675 PVC/CO₃-LDHs. Additionally, HPO₃-LDHs exhibit a synergetic interaction with zinc stearate to
 676 maintain the long-term stability of PVC, which is explained by the fact that HPO₃⁻ ions react with
 677 ZnCl₂ to generate zinc phosphate, suppressing the “zinc burning”.



678 Fig. 17 (a) Pictures of the PVC sheets recovered after heat-resistance test at 180 °C. (a) PVC, (b) PVC/MgAl-CO₃-LDH, (c)
 679 PVC/[Mg-Al-CO₃-LDH + Dpe], (d) PVC/MgAl-LDH-Dpe, (e) PVC/LiAl-LDH-Dpe, and (f) PVC/C18M; (b) Time dependence on
 680 hardness of the PVC sheets recovered after the heat-resistance test at 180 °C. Reprinted with permission from (Aisawa et al., 2019).
 681
 682

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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

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

723

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730

731 **References**

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