

Layered Double Hydroxide/NaSb(OH)₆-Poly(vinyl chloride) Nanocomposites: Preparation, Characterization, and Thermal Stability

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ABSTRACT: A novel layered double hydroxide/NaSb(OH)₆-based nanocomposite (Sb-LDH) has been prepared via intercalation of thio-antimonite (SbS₃³⁻) and reconstruction of LDH using Mg-Al LDH as precursors. It is composed of LDH nanolayers with thickness of 25 nm and NaSb(OH)₆ nanoparticles with diameter of 3–25 nm. The presence of NaSb(OH)₆ will decrease the decomposition intensity and hinder the decomposition of Mg-Al LDH because of the potential synergetic effect. When applied to poly(vinyl chloride) (PVC) composites, both Mg-Al LDH and Sb-LDH can enhance the thermal stability and increase the decomposition temperature of PVC. Compared with Mg-Al LDH, Sb-LDH results in higher decomposition temperatures and whiteness and higher initial and long-term stabilities due to the pres-

ence of NaSb(OH)₆, which can react with HCl and coordinate with Cl in the PVC chains. Because Mg-Al LDH will accelerate the dehydrochlorination of PVC driving by the Lewis acid such as AlCl₃, the thermal stability of PVC decreases with increasing nanofiller loading. When 1 wt % Sb-LDH was added, the color change time and Congo red time of PVC composites are 140 min and 154 min, respectively. With enhanced thermal stabilization, this novel LDH nanocomposite could gain promising application in thermal stabilizer for PVC resins. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1977–1984, 2010

Key words: layered double hydroxide (LDH); additives; nanocomposites; stabilization; poly(vinyl chloride) (PVC)

INTRODUCTION

Poly(vinyl chloride) (PVC) is a widely used commodity polymer and has applications in many fields such as water pipes, flooring, and sheets.¹ It has advantages of high wear resistance, high strength, electrical insulation, resistant to chemical corrosion, low production cost, and so on.^{1,2} However, due to its high chloride content (56.8%), PVC is unstable when exposed to high temperature, UV light, or ozone by participating in an autocatalytic dehydrochlorination reaction,³ which degrades PVC properties. To enhance the thermal stability of PVC, various kinds of additives have been investigated in the past years, among which lead salts, metal soaps, and organotin compounds⁴ are prominent. The lead salts have excellent stabilization effect and low production costs but are toxic that may cause environmen-

tal pollution. The metal soaps have good transparency and lubricity for plastics, but the stabilization effects are usually low and vary with metal types. Organotin stabilizer is highly efficient and generally not toxic, but the highly production cost restricts its applications.⁴ With the worldwide demand of environmental protection, researches are focused on efficient, low cost, and nontoxic thermal stabilizers for PVC.

Layered double hydroxides (LDHs), also known as hydrotalcite and hydrotalcite-like compounds, are a class of nontoxic and environmentally friendly anionic clays. The general formula of LDHs is [M_{1-x}^{II}M_x^{III}(OH)₂](Aⁿ⁻)_{x/n}·mH₂O, where M^{II} and M^{III} represent the divalent and trivalent metal cation in the structural layer, and Aⁿ⁻ stands for the changeable interlayer anions.⁵ Because of their layered structure, high changeability of layer cations and interlayer anions, high changeability of crystal size and distributions, LDHs have been used in various fields, such as adsorbents,⁶ electrochemical materials,⁷ magnetic materials,^{8,9} optical materials,¹⁰ catalysts,¹¹ flame retardants,^{12–14} and drug-releasing

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materials.¹⁵ In particular, because LDHs can absorb the HCl that released from the dehydrochlorination of PVC and, thus, hinder the autocatalytic dehydrochlorination reactions, LDHs are found to be efficient additives to enhance the thermal stability of PVC. LDHs with different layer cations and inter-layer anions have been prepared and applied to PVC resins to improve both the initial and long-term thermal stabilizations of PVC.^{16–18}

Antimony compounds, including inorganic and organo antimony compounds, occupy an important position in the field of thermal stabilizer for PVC resins. They have advantages of highly efficient, low cost, good gloss stability, and low melting viscosity.^{19,20} However, the disadvantages such as high density, low transparency, labile and susceptible to sulfur hindered the development of antimony stabilizer. Nowadays, antimony stabilizers are merely suitable for some deep-colored materials, such as disc, sewer pipe, and oil pipeline.

Recent studies suggest that antimony stabilizer has synergetic effect with some other stabilizers such as metal soaps, and incorporation of guest species into a layered host will often present synergetic behavior and enhanced physic-chemical properties.^{21–23} Herein, we prepared a novel Mg-Al LDH/NaSb(OH)₆ nanocomposite (Sb-LDH) via intercalation of SbS₃³⁻ and reconstruction of LDHs. It is composed by Mg-Al LDH nanolayers and NaSb(OH)₆ nanoparticles with 3–25 nm in diameter. The presence of NaSb(OH)₆ can increase the decomposition temperatures and decrease the decomposition intensities of Mg-Al LDH. When applied to PVC resins, we examined the color and transparence of PVC/Mg-Al LDH and PVC/Sb-LDH composites as a function of nanofiller loading, and systematically investigated and compared the thermal stabilities and thermo gravimetric (TG) properties of PVC/Mg-Al LDH and PVC/Sb-LDH composites.

EXPERIMENTAL

Materials

Mg-Al LDH with formula of Mg₆Al₂(OH)₁₆CO₃·4H₂O was purchased from Jiangsu Ruijia Chemistry (Yixing, China). Stibnite containing 99.8 wt % Sb₂S₃ was supplied by Xikuangshan Mining Bureau (Loudi, China). Na₂S, Na₂CO₃, paraffin, diisooctyl phthalate (DIOP), and stearic acid were purchased from Sinopharm Chemical Reagent (Shanghai, China). Unstabilized PVC with *K*-value of 66–68 was supplied by department of polymer, Zhejiang University. All chemicals were used as received without further purification.

Preparation of Sb-LDH

In a typical procedure, 50 g powdered stibnite (containing 99.8 wt % Sb₂S₃) with diameter of less than 150 μm was added into 500 mL of 8% Na₂S solutions and stirred for 2 h. After filtering the insoluble residues, 150 g calcination (550°C for 5 h) product of Mg-Al LDH was added into the 3–4 times-diluted filtrate with pH of 8–9 and stirred at 90°C for 2 h. The obtained precipitate (named SbS₃-LDH) was filtered, washed thoroughly by deionized water, dried at 90°C, and recalced at 600°C for 5 h. After cooled to room temperature naturally, 30 g calcination product was poured into 1 L of 1 mol L⁻¹ Na₂CO₃ aqueous solutions and stirred for 12 h at room temperature. After separation by centrifugation, it was washed thoroughly and dried at 90°C; Sb-LDH was prepared.

Preparation of PVC/Sb-LDH and PVC/Mg-Al LDH composites

All compositions (40 g PVC, 24 g DIOP, 0.2 g paraffin, 0.2 g stearic acid, and certain amounts of Mg-Al LDH or Sb-LDH) were melt compounded with a two-roll mill at 165°C for 5 min. The obtained product was then molded into sheets with thickness of 2 mm using a laboratory press at 165°C and 14 MPa for 5 min. According to the mass percent of Mg-Al LDH or Sb-LDH to PVC, the PVC composites were named L-1–L-20 (PVC/Mg-Al LDH composites) and S-1–S-20 (PVC/Sb-LDH composites).

Characterization

The elemental contents of Sb-LDH were examined by a INCA Energy X-ray energy spectrometer (EDS, Oxford). The color and transparence of samples were determined by a qingtong YQ-Z-48A whiteness determinator (Hangzhou, China) according to the China national standard GB 2913-82. The ratios between the radiant energy of specified blue-light diffuse reflection on the plastic surface and on the ideal condition were recorded as the whiteness and transparence of samples. The structure of samples was characterized by a D/max 2550 X-ray diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda = 0.15406$ nm) at a scan rate of 0.02°·s⁻¹. The morphologies of samples were characterized by a Philips CM200UT transmission electron microscope (TEM) at an accelerating voltage of 160 kV.

The thermal stabilities of PVC/Mg-Al LDH and PVC/Sb-LDH composites were determined by Congo red method, thermal aging test, and TG analysis. The procedure for Congo red method is described in ISO standard 181-1 : 1990. The time that elapsed to observe a color change from red to blue

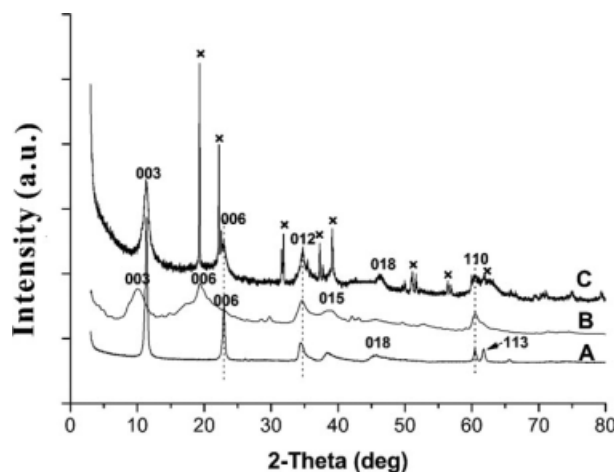


Figure 1 X-ray diffraction (XRD) patterns of (A) Mg-Al LDH, (B) SbS₃-LDH, and (C) Sb-LDH.

on Congo red paper was determined when a PVC composite resin was heated at 180°C. The thermal aging test was carried out by adding 1 × 1 cm strips into a thermal aging test box at 180°C ± 1°C according to ISO standard 305-1990. The TG experiments were conducted on a SDT Q600 (AT, USA) thermal analysis system with a heating rate of 10°C min⁻¹ under air atmosphere.

RESULTS AND DISCUSSION

Characterizations of Sb-LDH

The XRD patterns of the precursor Mg-Al LDH and the derivative SbS₃-LDH and Sb-LDH are shown in Figure 1. All the samples present a set of diffraction peaks that can be indexed as hexagonal layers. The d_{003} spacing that represents the interlayer spacing of Mg-Al LDH is 0.777 nm, which is equal to the reported data of Mg₆Al₂(OH)₁₆CO₃·4H₂O.²⁴ After calcination and reaction with SbS₃³⁻, the d_{003} spacing of the obtained SbS₃-LDH was increased to 0.866 nm, suggesting that SbS₃³⁻ has been successfully intercalated into the interlayer of LDH. Subsequently, SbS₃-LDH was calcined, and SbS₃³⁻ was oxidized to Sb₂O₅ and coexisted with LDO (reaction 1). Finally during the Na₂CO₃ treatment, Mg-Al LDH was reconstructed through the “memory effect” of LDO, that is, LDO can easily reconstruct the original layered structure in an aquatic environment, and NaSb(OH)₆ was simultaneously formed on the layers of Mg-Al LDH by the reactions between Sb₂O₅ and NaOH (reaction 2). As a result, the final product—Sb-LDH shows a d_{003} spacing of 0.777 nm and a set of peaks that marked with “x” in the XRD pattern, which can be assigned to tetragonal NaSb(OH)₆ (JCPDF#85-0363) with characteristic lattices of (111), (200), and (202). Note that all three samples present an identical d_{110} spacing (0.153 nm), suggesting

that the structural composition of LDHs does not change during the synthesis of Sb-LDH. The formation route and structural formula of Sb-LDH can be further proved by the energy spectrum analysis of Sb-LDH, where mass fractions of Mg, Sb, Al, Na, C, and O are 18.8, 10.5, 6.9, 2.0, 1.7, and 56.5%, respectively.

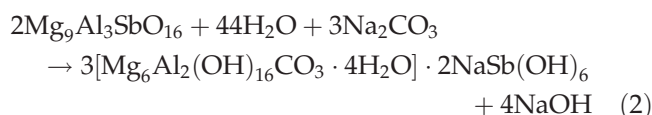
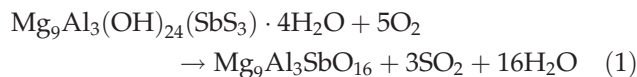


Figure 2 shows the TEM images of Sb-LDH. Under low magnification of 16,000, Sb-LDH shows typically layered appearance that belonged to Mg-Al LDH, and no other morphologies can be found [Fig. 2(A)]. The diameter and thickness of these LDH layers are 80–300 nm and around 25 nm, respectively. When the magnification of TEM was increased to 54,000, however, massive black dots are present on the layers of Mg-Al LDH [Fig. 2(B)]. These black dots are in uneven distribution and vary from 3 to 25 nm in diameter [shown in Fig. 2(D)], showing a mean diameter of 7 nm. The high-resolution TEM (HRTEM) pattern revealed that the typical lattice spacing of the black dot is 0.458 nm [Fig. 2(C)], which is identical with the d_{111} spacing of NaSb(OH)₆ crystal. The XRD and TEM characterizations indicate that we have successfully prepared a novel LDH/NaSb(OH)₆ nanocomposite, which consists of Mg-Al LDH nanolayers and NaSb(OH)₆ nanoparticles with diameters of 3–25 nm.

Figure 3 presents the TG, DTG, and DTA curves of Sb-LDH and Mg-Al LDH. Both Mg-Al LDH and Sb-LDH exhibit a two-step weight-loss process. The first step is attributed to the loss of bound water in the interlayer space of LDHs. It appears at below 220°C and decreases 11.92 wt % of Sb-LDH and 16.11 wt % of Mg-Al LDH. The maximum decreasing rates of weight-loss (T_{max}) at this step are 205°C for Mg-Al LDH and 210°C for Sb-LDH. The second weight-loss process starts at above 250°C and is attributed to the simultaneous dehydroxylation and decarbonation of the lattice of LDH. It reduces 19.68 wt % of Sb-LDH and 27.05 wt % of Mg-Al LDH. In this step, the T_{max} of Mg-Al LDH and Sb-LDH is 381°C and 392°C, respectively. The TG behavior of Sb-LDH confirmed the reaction mechanism and structural formula of Sb-LDH that was suggested in the former sections.

Compared with Mg-Al LDH, Sb-LDH shows smooth TG and DTG curves and lower endothermic

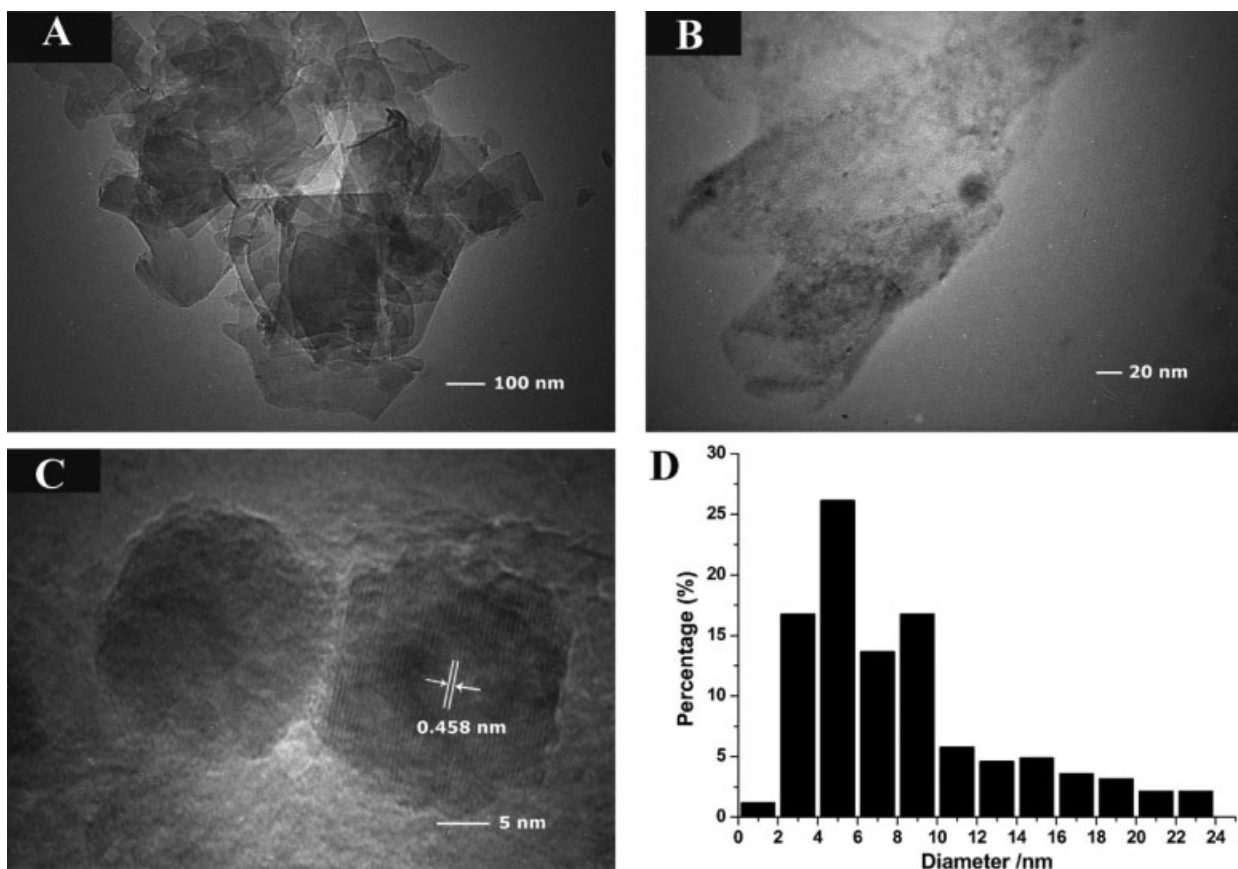


Figure 2 TEM images of Sb-LDH: TEM images under magnification of (A) 16,000, (B) 54,000, (C) HRTEM pattern at magnification of 450,000, and (D) particle size distribution of NaSb(OH)₆ in Sb-LDH.

values. The residue content of Sb-LDH at 800°C (64.3%) is higher than that of LDH (53.9%). It is attributed to the presence of NaSb(OH)₆ nanoparticles, which will reduce the weight ratio of bound water and CO₃²⁻ in Sb-LDH, since NaSb(OH)₆ will not decompose until 1427°C. In addition, Sb-LDH presents higher T_{\max} temperatures than Mg-Al LDH for every decomposition steps, indicating that the presence of NaSb(OH)₆ will delay the decomposition of LDH. Possibly, there are synergetic effects that stabilized the structure and hindered the decomposition of LDH between NaSb(OH)₆ and Mg-Al LDH.

Color and transparence of PVC composites

Color and transparence are important parameters for PVC products. Plastic with light colors and high transparence is easy to be tailored to fulfill different demands on color and transparence. Figure 4 shows the color and transparence of PVC/Mg-Al LDH and PVC/Sb-LDH composites. It can be seen that without Mg-Al LDH or Sb-LDH added, PVC is not stable and decomposes even under milling, resulting in a yellow PVC resin with whiteness of only

3.15% and transparence of 66.96%. When 1 wt % Mg-Al LDH or Sb-LDH was added, the whiteness of PVC resins increases immediately to 22.7% (L-1) and 37.6% (S-1) because of the improved thermal stability. Thereafter, however, the whiteness starts to decline as the loading of Mg-Al LDH or Sb-LDH increases. Likewise, the transparence of PVC composites increases with the loading of Mg-Al LDH or Sb-LDH first. When the loading was greater than 1 wt % or 2.5 wt %, the transparence starts to decrease and even lower than that of PVC resin without stabilizer added. These results are ascribed to the fact that Mg-Al LDH will absorb the HCl that released from PVC and hence hinder the autocatalytic dehydrochlorination of PVC that is driven by HCl. However, the resulting Lewis acid such as AlCl₃ will promote the dehydrochlorination. The promoting effect predominates gradually with the increasing of Mg-Al LDH, resulting in deeper colors.²⁵ NaSb(OH)₆ can also absorb HCl, and the resulting product cannot accelerate the dehydrochlorination of PVC. Moreover, the presence of NaSb(OH)₆ will decrease the transparence, enhance the thermal stability of Mg-Al LDH, and decrease the weight ratio of Mg-Al LDH. As a result, the

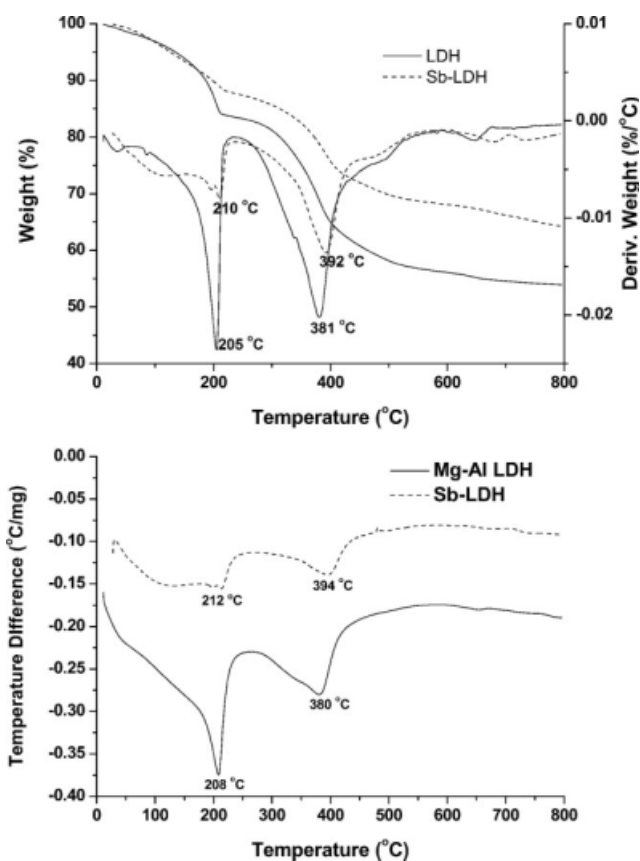


Figure 3 TG, DTG, and DTA curves of Sb-LDH and Mg-Al LDH.

addition of Sb-LDH results in PVC resins with higher whiteness and lower transparency compared with Mg-Al LDH.

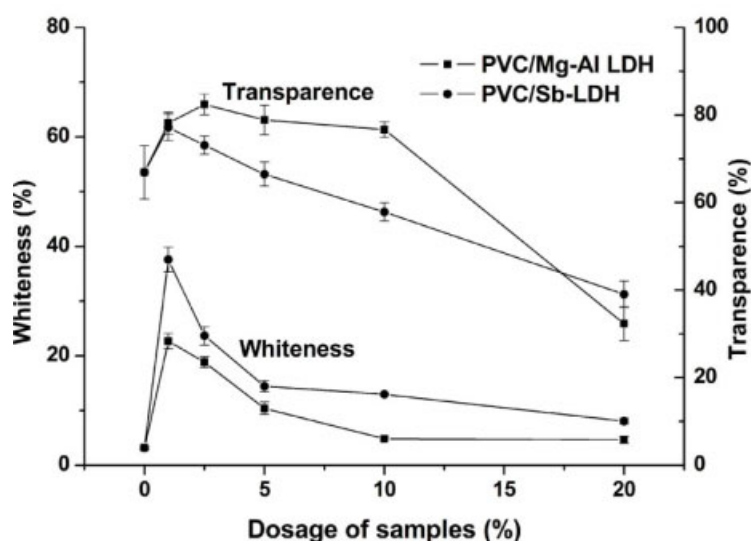


Figure 4 Left part: effect of nanofiller loading on the color and transparency of PVC/Sb-LDH and PVC/Mg-Al LDH composites. Right part: corresponding photos of (PVC) PVC resins without stabilizers added, (S-1-S-20) PVC/Sb-LDH composites, and (L-1-L-20) PVC/Mg-Al LDH composites. The photos are taken by a Cannon A550 digital camera on PVC composites with thickness of 2 mm. The PVC resins cover a white paper with black letters of "ZJU" drawing by a marker pen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal decomposition of PVC composites

The TG and DTG analysis of PVC/Mg-Al LDH and PVC/Sb-LDH composites are shown in Figure 5. All the samples show a three-step weight loss process during the heating in air. The first step starts at below 200°C, reaches a maximum rate at about 300°C, and ends at about 350°C. This step is mainly attributed to the autocatalytic dehydrochlorination of PVC and dehydration of Mg-Al LDH. The plasticizer of PVC resins, DIOP, is also oxidized at this step. The second and third steps are relatively smooth and result from the dehydrocarbonation and oxidation of PVC and dehydroxylation and decarboxylation of the lattice of Mg-Al LDH.

When Mg-Al LDH or Sb-LDH was added into the PVC composites, the initial decomposition temperatures (T_1) of PVC resins increased dramatically at first. Because Mg-Al LDH can also accelerate the dehydrochlorination of PVC, T_1 started to decline when the nanofiller loading was greater than 2.5 wt %. Similarly, the maximum derivative weight loss (DTG_{max}) and T_{max} decreased first and increased afterward with the increase in nanofiller loading. The PVC/Sb-LDH composites present lower DTG_{max} and higher T_{max} and T_1 than those of PVC/Mg-Al LDH composites, attributed to the presence of NaSb(OH)₆ nanoparticles.

Thermal stabilities of PVC composites

When exposed to heat, PVC is unstable and will release HCl and form chromophoric groups such as polyene, leading to a color change of transparency

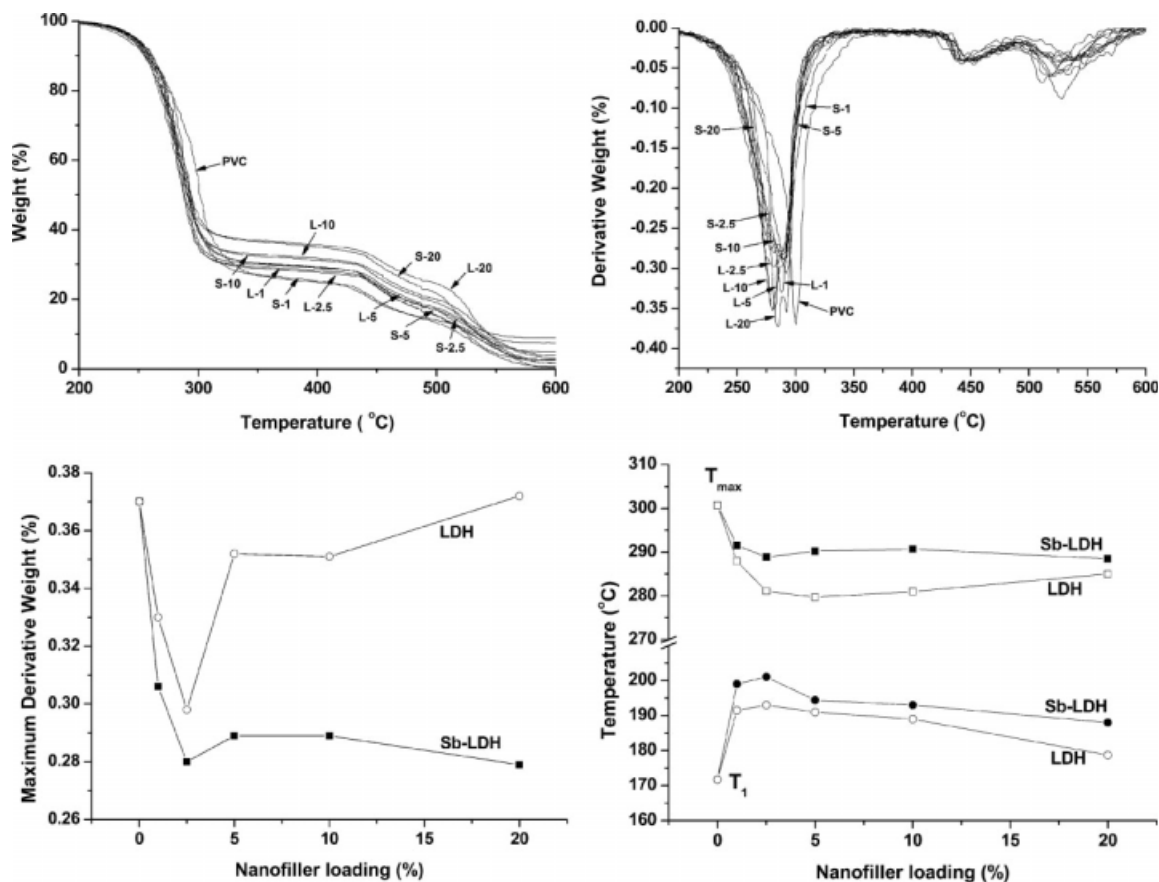


Figure 5 Effects of Mg-Al LDH and Sb-LDH on the thermal decomposition of PVC composites.

– light red – yellow – brown – black. Therefore, the thermal stabilities of PVC resins can be determined by examining the color change at intervals under heating. Figure 6 shows the color change of PVC/Mg-Al LDH and PVC/Sb-LDH composites. The PVC resin without stabilizer added turned black after less than 10 min. Because both Mg-Al LDH and Sb-LDH can enhance the thermal stability of PVC, the PVC composites except L-10 and L-20 exhibit a color change of yellow – brown – black as the heating continues. The color change time from yellow to brown and brown to black decreases with increasing nanofiller loading, and the PVC/Sb-LDH composites showed longer color change times than PVC/Mg-Al LDH composites.

In addition, we determined the thermal stabilities of PVC composites via Congo red method. Without stabilizer added, the Congo red paper turned blue only after 12.5 min when heated at 180°C. When less than 2.5 wt % of Mg-Al LDH or Sb-LDH was added into the PVC composites, the color change of Congo red paper was very slow, and the Congo red time increases with the nanofiller loading. The test paper turned from red to purple first after 90 min (L-1), 104 min (S-1), 135 min (L-2.5), or 153 min (S-2.5). Afterward, it turned from purple to blue after 126

min (L-1), 154 min (S-1), 176 min (L-2.5), or 235 min (S-2.5). When the nanofiller loading was further increased, however, we cannot observe expected color changes even after 1 day when the test paper was used out.

From these results, we can conclude that Sb-LDH is an efficient thermal stabilizer for PVC. Compared with other thermal stabilizers such as metal soaps,²⁶ LDH with different compositions,¹⁷ and organic stabilizers,^{27–29} the color change times from white to black and the Congo red time of PVC/Sb-LDH composites are close or higher at low concentrations. However, both Mg-Al LDH and Sb-LDH are secondary stabilizers that react with HCl to delay the autocatalytic degradation but cannot protect against short time discoloration. As shown in Figure 5, the whiteness of PVC composites decreases with the increasing of nanofiller loading, indicating that more HCl was adsorbed and more PVC was dehydrochlorinated during the milling with increasing Mg-Al LDH. Therefore, the Congo red times increase, but the color change times from yellow to brown and brown to black decrease with increasing nanofiller loading. The residual HCl in L-5–L-20 and S-5–S-20 is not enough to change the color of test paper; we could not observe a color change consequently.

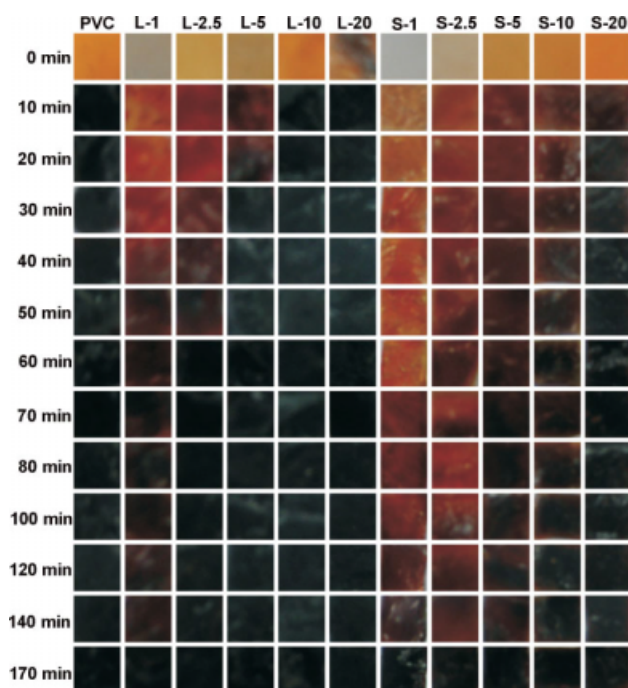


Figure 6 Thermal stabilities of PVC/Mg-Al LDH and PVC/Sb-LDH composites: (PVC) PVC resins without stabilizers added, (S-1–S-20) PVC/Sb-LDH composites, and (L-1–L-20) PVC/Mg-Al LDH composites. The photos are taken by a Cannon A550 digital camera. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Compared with PVC/Mg-Al LDH composites, PVC/Sb-LDH resins present lighter colors, higher static thermal aging times, and Congo red times. It is attributed to the presence of NaSb(OH)₆ nanoparticles that distribute on the layer of Mg-Al LDH. Antimony compounds are known as efficient thermal stabilizers for PVC. Inorganic antimony compounds such as Sb₂O₃ will react with HCl that released from the dehydrochlorination of PVC,³⁰ and the main stabilization effects of organo antimony are reacting with HCl and coordinating or substituting the Cl in the PVC chains.^{20,31,32} Likewise, the NaSb(OH)₆ nanoparticles can react with HCl that released from the decomposition of PVC and, thus, stabilized PVC. Second, the Sb in NaSb(OH)₆ is in dsp³ hybridization that can coordinate with the Cl in the PVC chains, and, thus, prevented the dehydrochlorination of PVC.²⁰ The initial stability of PVC resins was enhanced as a result. Furthermore, the presence of NaSb(OH)₆ will decrease the weight ratio of Mg-Al LDH and, thus, decrease the dehydrochlorination of PVC during the milling, leading to lighter colors. And at last, the presence of NaSb(OH)₆ will increase the initial decomposition temperatures of Mg-Al LDH and PVC composites (shown in Fig. 3 and Fig. 5), and as a result the long-term stability of PVC composites was enhanced.

CONCLUSIONS

In summary, we have successfully prepared a LDH/NaSb(OH)₆ nanocomposite (Sb-LDH), which consisted of Mg-Al LDH nanolayers and NaSb(OH)₆ nanoparticles via intercalation of SbS₃³⁻ and reconstruction of Mg-Al LDH. Both Mg-Al LDH and Sb-LDH can enhance the thermal stability of PVC composites. Because the presence of NaSb(OH)₆ can coordinate with the Cl in the PVC chains, decrease the weight ratio of Mg-Al LDH, and increase the initial decomposition temperatures of Mg-Al LDH and PVC resins, the PVC/Sb-LDH composites show higher initial stability and long-term stability than that of PVC/Mg-Al LDH resins. Nevertheless, there are still some limitations in this research. The investigations on the synergetic effect between Mg-Al LDH and NaSb(OH)₆ and the preparation of other LDH nanocomposites with thermal stabilization effect are being studied.

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