

## Thermal Stability and Thermal Aging of Poly(vinyl chloride)/MgAl Layered Double Hydroxides Composites\*

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**Abstract** MgAl-LDH (layered double hydroxides) were prepared with  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3\cdot\text{H}_2\text{O}$  by the co-precipitation method, respectively. Corresponding composite membranes were prepared by the coating method. LDHs were characterized by WAXS,  $\text{CO}_2$ -TPD and SEM. The morphology of the PVC/LDHs composite membranes were characterized by means of SEM. The thermal stability of the membranes was analyzed by air aging box and TGA-FTIR. The SEM results show that nano-particles can be compatible with poly(vinyl chloride) (PVC) matrix homogeneously by the stirring-ultrasound blend method with two steps. Furthermore, the air aging box results proved that MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH has the best effect on thermal stability of PVC. TGA-FTIR results show that MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH could adsorb more HCl that resulted from the degradation of PVC and improve the pyrolysis temperature of the first degradation stage by 15 K compared with PVC.

**Keywords:** Poly(vinyl chloride); Layered double hydroxide; Thermal stability; TGA-FTIR.

### INTRODUCTION

Poly(vinyl chloride) (PVC) is a type of thermoplastic polymer which is very widely used in many fields, such as water pipes, floor and roof tiles, packing films and sheets because of its easy processing, good mechanical properties, and low production cost<sup>[1]</sup>. However, it is well known that PVC is very unstable and easy to degrade when exposed to heat, shear or radiation (such as ultraviolet (UV) light) during melt-processing and practical applications due to an autocatalytic dehydrochlorination degradation reaction<sup>[2, 3]</sup>. So it is necessary to add thermal stabilizers to improve its thermal stability. The increasing public awareness of environmental issues in the world results in a shift of thermal stabilizers towards the nontoxic, environmentally friendly, and high-efficiency system<sup>[4, 5]</sup>. Therefore, metal soaps, rare earth stabilizers, hydrotalcite like materials, and other nontoxic thermal stabilizers have played an important role in this field<sup>[6]</sup>.

LDHs are a class of anionic-exchanging layered materials. The structure of LDHs is based on positively charged brucite-like sheets and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions<sup>[7, 8]</sup>. Due to their acidic and alkaline characteristics, memory effect, large surface area, high anion exchange, and good thermal stability, LDHs have become a new material with great research potential and

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application prospect such as nanocomposite hydrogels<sup>[9]</sup>, UV-light shielding<sup>[10]</sup>, rheology<sup>[11]</sup>, oil enhanced recovery<sup>[12]</sup> *et al.*<sup>[13, 14]</sup>. LDHs have much higher charge densities in the interlayer than other common inorganic layered materials such as clay<sup>[15, 16]</sup>. In recent years, the addition of LDHs in PVC matrix to prepare PVC/LDHs composites has attracted much interests. For example, Liu *et al.*<sup>[3, 17]</sup> obtained poly(vinyl chloride)/layered double hydroxide nanocomposites by melt intercalation or solution intercalation process and reviewed the recent research progress of PVC/LDHs nanocomposites.

Considering the thermal stability and compatibility of hydrotalcites for PVC, LDHs must be modified. Nitrogenous compounds are often used to eliminate odors that resulted from the thermal stabilizers used in PVC. Meanwhile, urea or ammonium carbonate hydrolysis reactions are also used to generate hydroxyls *in situ*<sup>[18, 19]</sup>. Therefore, in our recent work<sup>[20]</sup>, we reported the structural characterization of Mg-Al LDHs which synthesised by decomposition of ammonium compounds and urea. The structure, morphology, basicity and thermal stability were studied by XRD, FTIR, SEM, CO<sub>2</sub>-TPD and TG. It was found that the calcined samples show a relatively high surface area and total pore volume. As is well known, thermogravimetric analysis (TGA) is an important technique to study the thermal stability<sup>[21, 22]</sup>. In this article, the effect of the dispersed LDHs particles on PVC thermal stability is reported in detail by TGA-FTIR in nitrogen<sup>[23, 24]</sup>. As thermooxidative degradation process in air is more complex than thermal degradation in nitrogen, the discoloration method was employed to prove the isothermal thermooxidative degradation mechanism of PVC.

## EXPERIMENTAL

### Preparation of Intercalated MgAl-LDH and PVC/LDHs Composite Membranes

Mixed salt solutions containing Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and CO(NH<sub>2</sub>)<sub>2</sub>, NH<sub>4</sub>Cl or NH<sub>3</sub>·H<sub>2</sub>O (with solution concentration of 0.03 mol/L, 0.01 mol/L and 0.02 mol/L, respectively), and a mixed solution containing NaOH and Na<sub>2</sub>CO<sub>3</sub> (with solution concentration of 0.01 mol/L and 0.005 mol/L respectively) were synchronously added slowly to the deionized water at a speed of 1 drop/s, respectively, under vigorous stirring at 60 °C. The mixture was stirred for 4 h with a constant pH = 10. The precipitate was then filtered and washed with deionized water. Finally, the precipitate was grinded to fine powder after drying<sup>[25, 26]</sup>.

PVC/LDHs blends of different composition (*i.e.* 100/5% wt/wt) were fabricated as follows. PVC and LDHs granules powder were dissolved in THF in the chosen concentration, the overall polymer amount was kept 20% W/V. After magnetic stirring at room temperature, the solutions were poured in a filming coating machine. The schematic illustration of the formation process of PVC/LDHs composites is shown in Fig. 1.

All membrane samples were dried under vacuum for 24 h and stored in a dessicator.

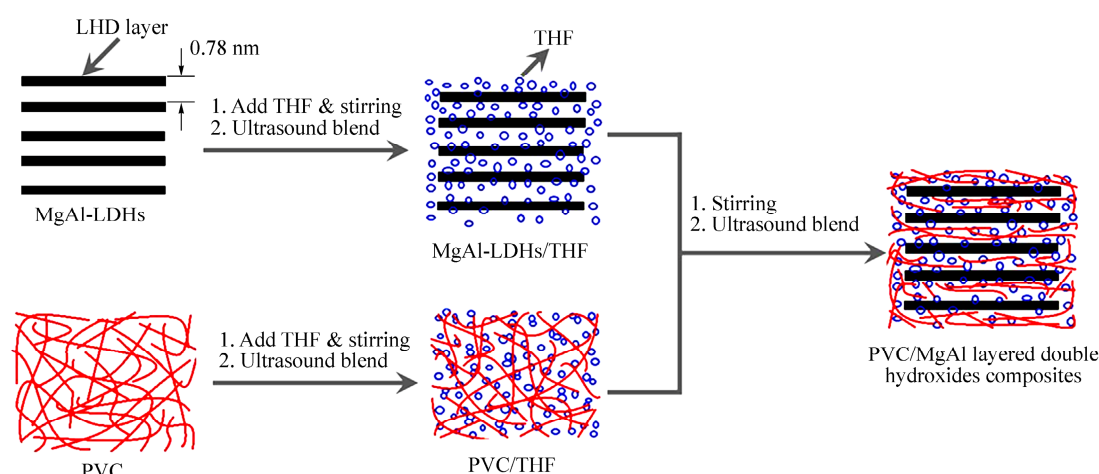


Fig. 1 Schematic illustration of the formation process of PVC/LDHs composites

### Characterization Techniques for LDHs and PVC/LDH Composite Membranes

The as-prepared LDHs were characterized with a scanning electron microscope (SEM; SU8010). Wide-angle X-ray scattering (WAXS) patterns were acquired from the beamline 7.3.3 of Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL). The basicity of the samples was determined by means of temperature programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD) with employing an AutoChemII2920 device. A  $\text{CO}_2$ -He gas mixture was employed as the analytical gas. The samples were saturated with  $\text{CO}_2$  gas. Desorption of carbon dioxide was performed after the system with the carrier gas at an increasing temperature from 50 °C to 500 °C with a heating rate of 10 K/min.

PVC/LDHs composite membranes were characterized with TGA-FTIR and thermal aging test. The TG-FTIR apparatus consisted of an SII TGA/DTA6300 thermogravimetry analyzer coupled with a Nicolet IS10 Fourier transform spectrometer for the analysis of evolved gases and the TGA-FTIR transfer line. The tests were carried out under nitrogen atmosphere at a flow rate of 50 mL/min for TG, the temperature was set from room temperature to 700 °C, with a heating rate of 10 K/min. The FTIR spectral region was set as 4000–400  $\text{cm}^{-1}$ . The temperature of air aging box was  $(190 \pm 2)$  °C, a piece of the PVC/LDHs composite membrane was taken out every 10 min.

## RESULTS AND DISCUSSION

### Characterization of LDHs

#### WAXS analysis

As is shown in Fig. 2, the  $Q$ -data displayed at the (003) plane show peaks from MgAl-LDH, MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH, MgAl- $\text{NH}_4\text{Cl}$ -LDH and MgAl- $\text{NH}_3 \cdot \text{H}_2\text{O}$ -LDH at 8.2, 8.0, 7.9 and 7.9  $\text{nm}^{-1}$ , respectively<sup>[27, 28]</sup>. This indicates the basal spacing of 0.76, 0.78, 0.79 and 0.78 nm under ambient conditions. In juxtaposition with MgAl-LDH, the basal spacing of MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH, MgAl- $\text{NH}_4\text{Cl}$ -LDH and MgAl- $\text{NH}_3 \cdot \text{H}_2\text{O}$ -LDH increases. According to ion-exchange principles, anions will be exchanged into the interlayer and cations will be located at the layers of LDHs. Therefore,  $\text{CO}_3^{2-}$  is intercalated into the interlayer of LDHs and this leads to the increase of  $\text{CO}_3^{2-}$  concentration. According to literature, the small peak between (003) and (006) on the spectra results from the presence of carbonate impurities, which is also the reason for the small peak in MgAl-LDH as well. In short, the addition of  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  increases the basal spacing of LDH. This could be due to the reactions between  $\text{NH}_4^+$  and  $\text{OH}^-$  as well as  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and metal cations on the layers of LDH for MgAl- $\text{NH}_4\text{Cl}$ -LDH and MgAl- $\text{NH}_3 \cdot \text{H}_2\text{O}$ -LDH. Nevertheless, addition of  $\text{CO}(\text{NH}_2)_2$  makes more  $\text{CO}_3^{2-}$  intercalated into the interlayer of LDHs<sup>[29, 30]</sup>.

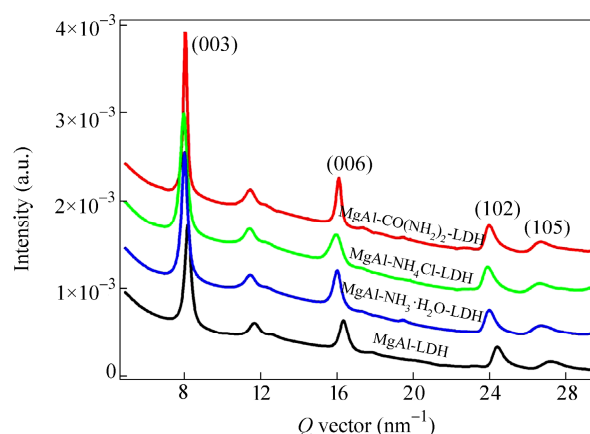


Fig. 2 WAXS patterns of LDHs samples

### CO<sub>2</sub>-TPD

The basicity of LDHs was tested through the temperature-programmed desorption of CO<sub>2</sub>. The CO<sub>2</sub> evolution, as a function of temperature, of MgAl-LDH, MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, MgAl-NH<sub>4</sub>Cl-LDH and MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH is depicted in Fig. 3. The CO<sub>2</sub> desorption peaks were observed in the temperature range of 100–500 °C, indicating the different types of basic sites with different basicity strength in the catalysts. The CO<sub>2</sub> desorption peak near 170–200 °C was attributed to the weak basic sites, while those near 225–235 °C and 390–400 °C were attributed to the moderate and strong basic sites, respectively. Weak basic sites were ascribed to OH<sup>−</sup> groups, moderate basic sites were related to Mg–O and Al–O pairs, and strong basic sites were associated with coordinatively unsaturated O<sup>2−</sup> ions<sup>[31, 32]</sup>. The range of 50–250 °C is the focus of discussion because the structure of layered double hydroxides changes in the range of 280–500 °C<sup>[33, 34]</sup>. Before 280 °C, two CO<sub>2</sub> desorption peaks were observed in the curves, including the different basic sites. Comparing with the sample MgAl-LDH its first peak is at about 194 °C, the MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH and MgAl-NH<sub>4</sub>Cl-LDH (180 °C) show weak basic sites, relatively. This could be related to NH<sub>4</sub><sup>+</sup> or NH<sub>3</sub>·H<sub>2</sub>O which reacted with OH<sup>−</sup> on the surface of LDH. MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH shows a stronger peak, which indicates it has a greater CO<sub>2</sub> absorption compared with MgAl-LDH at 194 °C. Specially, the second peak of MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH disappeared compared with other samples (230 °C), which could be attributed to that NH<sub>3</sub>·H<sub>2</sub>O could chelate metal cations on the layers of LDH. Consequently, the basicity of MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH and MgAl-NH<sub>4</sub>Cl-LDH was weakened. On the contrary, addition of CO(NH<sub>2</sub>)<sub>2</sub> improves the basicity of MgAl-LDH.

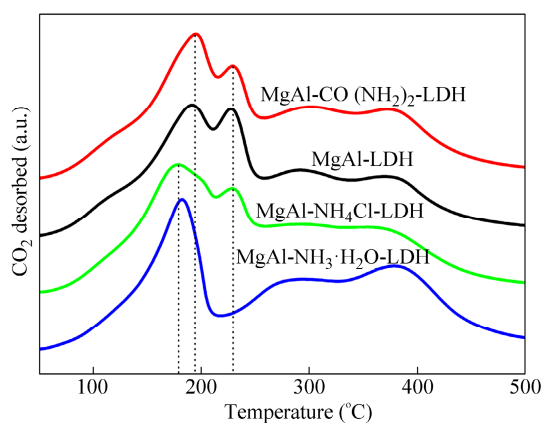


Fig. 3 Profiles of temperature-programmed desorption of CO<sub>2</sub> for different samples

### SEM analysis LDHs and PVC/LDHs

Typical SEM micrographs of LDHs are shown in Figs. 4(a), 4(b), 4(c) and 4(d), and those of PVC/LDHs composite membranes are shown in Figs. 4(A), 4(B), 4(C) and 4(D). Figures 4(a), 4(b), 4(c), 4(d) indicate the existence of lamellar (MgAl-LDH-CO(NH<sub>2</sub>)<sub>2</sub> is prominent), which is the common morphology of LDHs<sup>[35, 36]</sup>. As shown in Figs. 4(A), 4(B), 4(C) and 4(D), to a certain extent MgAl-LDH, MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH and MgAl-NH<sub>4</sub>Cl-LDH can be compatible with PVC matrix. Among them, the interface between MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH and PVC is the most fuzzy. Compatibility in descending order is MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, MgAl-NH<sub>4</sub>Cl-LDH, MgAl-LDH and MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH by observing their interfaces. The size of most nano-particles is about 200–500 nm. However, a little aggregation is observed, the size of which is about 800 nm in Figs. 4(B) and 4(C). This is due to the hydrogen bonding interaction among adjacent particles in the drying process.

### Thermal Aging Testing of PVC/LDHs Composites

PVC undergoes an autocatalytic dehydrochlorination reaction under heating. The effects of LDHs on the thermal stability of PVC are illustrated by observing the color of membranes during thermal aging tests. The thermal stability results for the PVC samples containing MgAl-LDH, MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH, MgAl-NH<sub>4</sub>Cl-LDH and MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH are shown in Fig. 5, respectively.

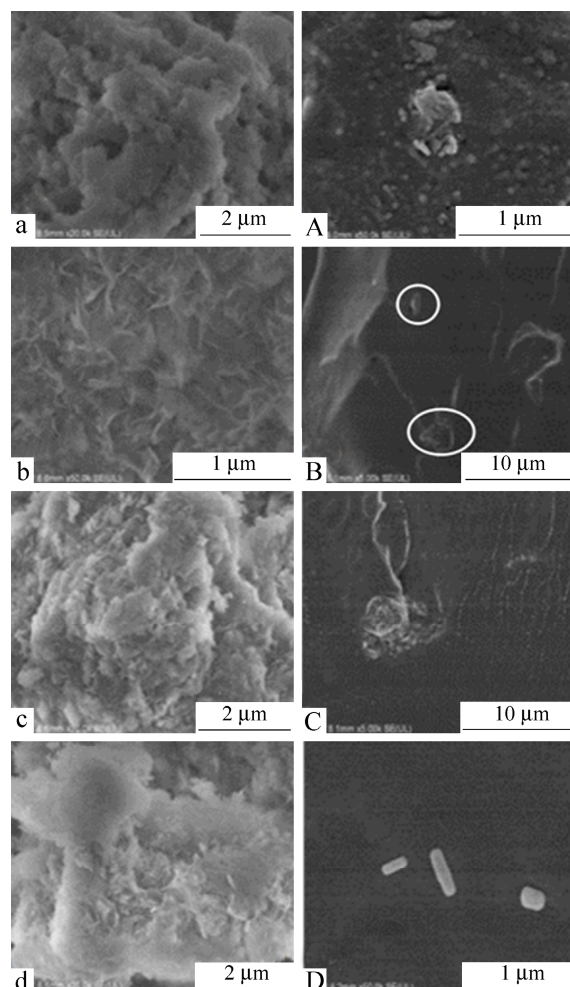


**Fig. 4** SEM images for LDHs and PVC/LDHs composite membranes: (a) MgAl-LDH, (b) MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, (c) MgAl-NH<sub>4</sub>Cl-LDH, (d) MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH, (A) PVC/MgAl-LDH, (B) PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, (C) PVC/MgAl-NH<sub>4</sub>Cl-LDH and (D) PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH

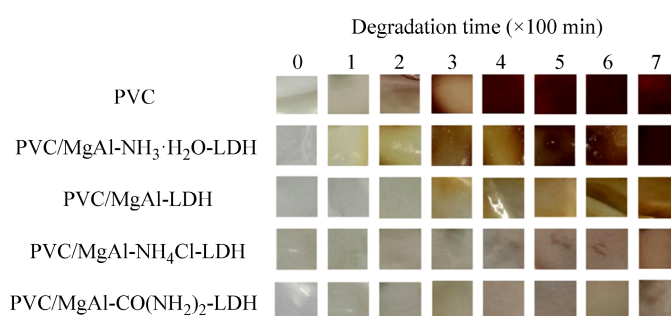


**Fig. 5** Discoloration tests for the degradation of composite membranes

As shown in Fig. 5, all the samples become darkened with time under the heating process, pure PVC without any stabilizer begins to color even during the mixing process and becomes brown in 20 min at  $(190 \pm 2) ^\circ\text{C}$ . The speed of color darkening for PVC/LDHs composites is slower than that for pure PVC, indicating the inorganic LDHs could delay the pyrolysis of PVC. As for PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH

composites, the color becomes brown at 60 min and 70 min, respectively. MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH has the best effect without a doubt. However, for the PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH, it is interesting that the color darkens at 20 min and it is darker than pure PVC at 70 min. When the color at 70 min is chosen for comparison, it can be observed that the PVC/MgAl-LDH, PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH composites have different colors and all are lighter than that of the pure PVC. At 70 min, they have the approximate color of the pure PVC at 30 min, 20 min, 10 min, respectively. In addition, some undissolved MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH particles and air bubbles were observed at 40 min and 60 min, respectively. NH<sub>3</sub>·H<sub>2</sub>O volatilizes and decomposes easily during heating. This result shows that NH<sub>3</sub> could not insert into MgAl-LDH and PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH could not compatible very well. While, the ions from NH<sub>4</sub>Cl or CO(NH<sub>2</sub>)<sub>2</sub> increase the compatibility between LDHs and PVC.

### TG-FTIR Analysis of PVC/LDHs Composites

The pyrolysis process of PVC can be divided into two stages. The major pyrolysis products of PVC in the first-stage (room temperature to 400 °C) are hydrogen chloride and chlorinated compounds. The pyrolysis products of the second-stage (400–700 °C) are very complicated. A substantial quantity of polyene sequences and some aromatic hydrocarbons are produced<sup>[37]</sup>. The effects of LDHs on thermal behavior for PVC mainly arise in the first stage. Therefore, the first stage of the PVC pyrolysis is the focus of discussion.

Figures 6 and 7 present the TG curves and DTG curves of PVC and PVC/LDH composites, respectively. The key parameters of the curves are summarized in Table 1. Similar to that of pure PVC, there are two major weight loss stages for the PVC/LDHs composites. It is observed that the thermal stability of PVC is improved with the addition of MgAl-LDH, MgAl-NH<sub>4</sub>Cl-LDH and MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH. From the TG curves and DTG curves, the following thermal characteristics can be determined: the onset degradation temperature ( $T_{on}$ ); the temperature of the maximum degradation rate of the first stage ( $T_{max}$ ), the temperature at 20 wt% weight loss ( $T_{20\%}$ ), and the residue yield at each stage ( $W_{res1}$ ,  $W_{res2}$ ).

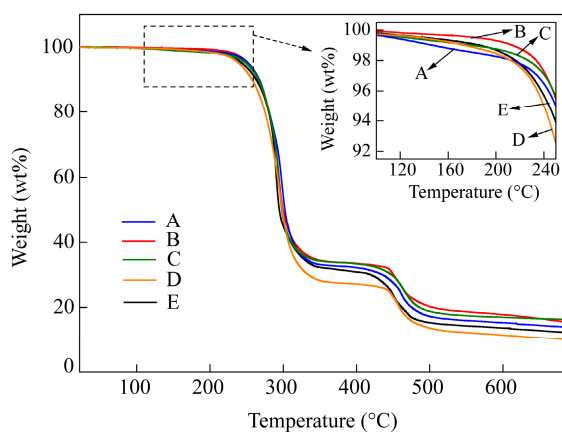


**Fig. 6** TG curves of LDHs and PVC/LDH composite membranes: (A) PVC/MgAl-LDH, (B) PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, (C) PVC/MgAl-NH<sub>4</sub>Cl-LDH, (D) PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH and (E) PVC

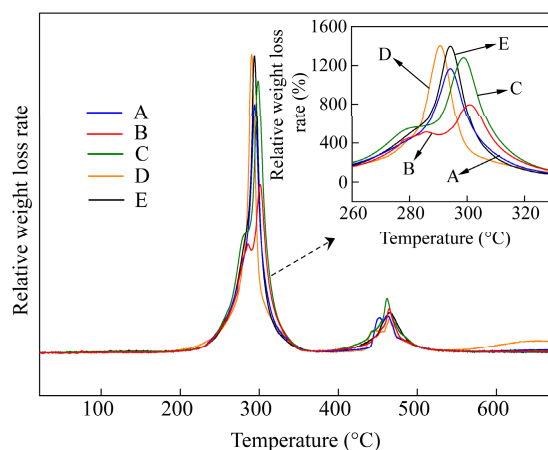


**Fig. 7** DTG curves of LDHs and PVC/LDH composite membranes: (A) PVC/MgAl-LDH, (B) PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, (C) PVC/MgAl-NH<sub>4</sub>Cl-LDH, (D) PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH and (E) PVC

The first stage of the composites can be attributed to hydrogen chloride produced in pyrolysis process of PVC. As shown in Table 1, the  $T_{on}$  and  $T_{max}$  increase from 215 and 292 °C to 222 and 294 °C respectively after addition of 5 wt% of MgAl-LDH. Furthermore, the residue yield of PVC/MgAl-LDH composite is 15.8 wt% larger than that of the pure PVC. This phenomenon results from the fact that LDHs themselves could contribute to the HCl adsorption and thus improve the thermal stability of PVC, although they are not dispersed very well.

**Table 1.** The TG results for the degradation of PVC, PVC/MgAl-LDH, PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH composites in nitrogen

| Materials                                      | $T_{on}$ (°C) | $T_{max}$ (°C) | $T_{20\%}$ (°C) | $W_{res1}$ (%) | $W_{res2}$ (%) |
|------------------------------------------------|---------------|----------------|-----------------|----------------|----------------|
| PVC                                            | 215           | 292            | 458             | 31.1           | 14.2           |
| PVC/MgAl-LDH                                   | 222           | 294            | 470             | 32.4           | 15.8           |
| PVC/MgAl-LDH-NH <sub>3</sub> ·H <sub>2</sub> O | 213           | 290            | 456             | 27.3           | 12.1           |
| PVC/MgAl-LDH-NH <sub>4</sub> Cl                | 231           | 298            | 480             | 33.2           | 17.4           |
| PVC/MgAl-LDH-CO(NH <sub>2</sub> ) <sub>2</sub> | 233           | 301            | 491             | 33.6           | 18.5           |

Interestingly, the thermal stability of the PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH composites are improved further because the ions from NH<sub>4</sub>Cl or CO(NH<sub>2</sub>)<sub>2</sub> increase the compatibility of LDHs and PVC. The  $T_{on}$ ,  $T_{max}$ ,  $W_{res1}$  and  $W_{res2}$  of PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH composites increase to 231 °C, 298 °C, 33.2 wt%, 17.4 wt% and 233 °C, 301 °C, 33.6 wt%, 18.5 wt% respectively, much higher than the corresponding values of the neat PVC. Hence, the thermal stability of PVC can be improved significantly with the MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH. Nevertheless, as for the PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH, it is interesting that the  $T_{on}$ ,  $T_{max}$ ,  $W_{res1}$  and  $W_{res2}$  reduce to 213 °C, 290 °C, and 27.3 wt% and 12.1 wt%, lower than those of the pure PVC. This is because NH<sub>3</sub>·H<sub>2</sub>O is decomposed before the  $T_{on}$  of PVC. In addition, the temperatures at 20% weight loss were chosen for comparison in Table 1. The results show that the  $T_{20\%}$  of PVC/MgAl-LDH, PVC/MgAl-NH<sub>4</sub>Cl-LDH and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH obviously increases as well, from 458 °C for PVC to 470 °C, 480 °C, and 491 °C, respectively. But for the PVC/MgAl-NH<sub>3</sub>·H<sub>2</sub>O-LDH, it reduces to 456 °C. Based on the earlier results, we may conclude that MgAl-LDH, especially MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH, which can react with HCl, have an important effect on delay of the pyrolysis process. All the involved reactions are given in sequence as follows:



The Eqs. (1)–(5) are the reactions, in which ammonia is generated by urea, and the Eq. (6) is the reaction of ammonium chloride. Urea produces more ammonia which can react with hydrogen chloride as the same amount of urea and ammonium chloride. While, NH<sub>3</sub>·H<sub>2</sub>O has volatilized and decomposed before the onset degradation temperature of PVC. Therefore, PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH composites have the best thermal stability.

The FTIR analysis was used to certify the interaction of PVC during the thermal decomposition process. Figure 8 shows the FTIR spectra of the evolved gas during temperature-programmed heating on PVC. The major pyrolysis products of PVC in the first-stage (0–38 min) was hydrogen chloride (asymmetrical stretching of H–Cl<sup>[38]</sup>) and chlorinated compounds, a small quantity of methylene (–CH<sub>2</sub>–) groups was detected from the bands related with the stretching of –C–H and scissoring of –CH<sub>2</sub>– bonds. The pyrolysis products of the second-stage (38–66 min) are very complicated. A substantial quantity of aromatic groups was detected according to the bands related with the stretching of Ph–H and stretching of –C=C–.

Figure 9 presents the FTIR spectra of the evolved gas of PVC and PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH at 292 °C ( $T_{max}$  of PVC). The compositions of pyrolysis products were complicated. Assignments of the IR bands to vibrational modes of atomic groups are shown in Table 2.

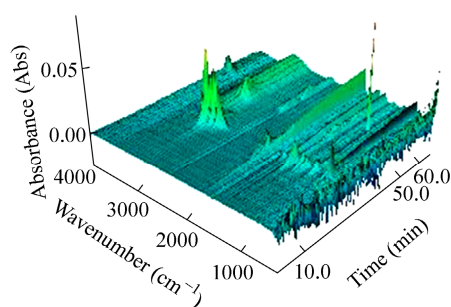


Fig. 8 3D-FTIR spectra of the evolved gas of PVC at a heating rate of 10 K/min

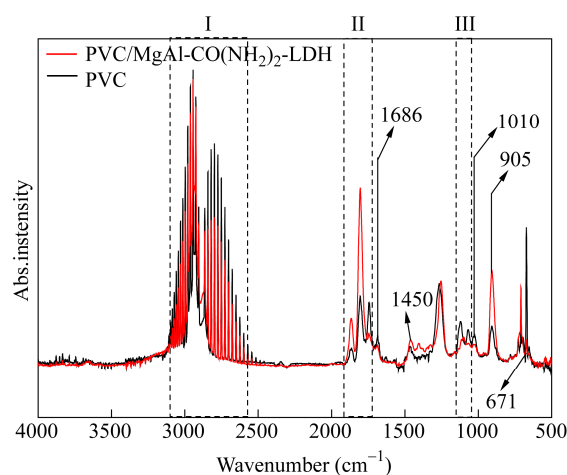


Fig. 9 FTIR spectra of the evolved gaseous of PVC at 292 °C

Table 2. The main functional groups identified by FTIR

| Group                | Vibrational mode | Assigned wavenumber (cm <sup>-1</sup> ) |
|----------------------|------------------|-----------------------------------------|
| C=C                  | Stretching       | 1700–1600                               |
| R-CH=CH <sub>2</sub> | Bending          | 1000–960, 940–900                       |
| H-Cl                 | Stretching       | 3100–2600                               |
| -CH <sub>2</sub> -   | Scissoring       | 1460                                    |
| -CH <sub>2</sub> -   | C-H stretching   | 3000–2700                               |
| -C-Cl                | Stretching       | 800–600                                 |

A broad absorption peak in 2600–3100 cm<sup>-1</sup> (as the Fig. 9-I) region is assigned to H-Cl group stretching. Meanwhile, the peaks in 1724–1921 cm<sup>-1</sup> (as the Fig. 9-II) and 1008–1150 (as the Fig. 9-III) regions are assigned to the chlorinated compounds based on OMNIC (infrared analysis software) standard spectra. A sharp absorption peak at 671 cm<sup>-1</sup> was assigned to the stretching of C-Cl bond. Obviously, this can verify that PVC produces more hydrogen chloride, while PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH produces more chlorinated compounds in the process of their pyrolysis, respectively. The C-Cl bond in the PVC structure has relatively lower bond energy than the C-C and C-H bonds. It shows clearly that, when the PVC is pyrolyzed, the chemical bonds of C-Cl will break with priority, which leads to the pyrolysis of PVC. In this sense, the addition of MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH improves the flame retardancy of PVC in the first stage without fracture of C-Cl bonds from chlorinated compounds produced by PVC/MgAl-CO(NH<sub>2</sub>)<sub>2</sub>-LDH. In addition, the bands of stretching of -CH<sub>2</sub>- (1450 cm<sup>-1</sup>), stretching of -C=C- (1686 cm<sup>-1</sup>) and plane -CH- bending -C-CH<sub>2</sub> (905, 1010 cm<sup>-1</sup>) were assigned to the alkenes. This can verify that PVC loses hydrogen chloride and forms a conjugated polyene structure when heated.

Figure 10 shows the FTIR spectra of the evolved gas of PVC at different temperatures. As indicated above, the broad absorption peak in the 2600–3100  $\text{cm}^{-1}$  region is assigned to the H—Cl group stretching. The bands of gaseous HCl are observed gradually as the temperature increases. At 215 °C, characteristic peaks of infrared absorption correspond to hydrogen chloride arise for PVC. However, the characteristic peaks are not there for PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH. At 230 °C, characteristic peaks of infrared absorption correspond to hydrogen chloride arise for PVC significantly, while the characteristic peaks are not obvious for PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH. This suggests that MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH puts off the initial pyrolysis temperature of PVC. Therefore the addition of MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH improves the PVC decomposition temperature of the first stage by 15 K. The PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH showed the best thermal stability.

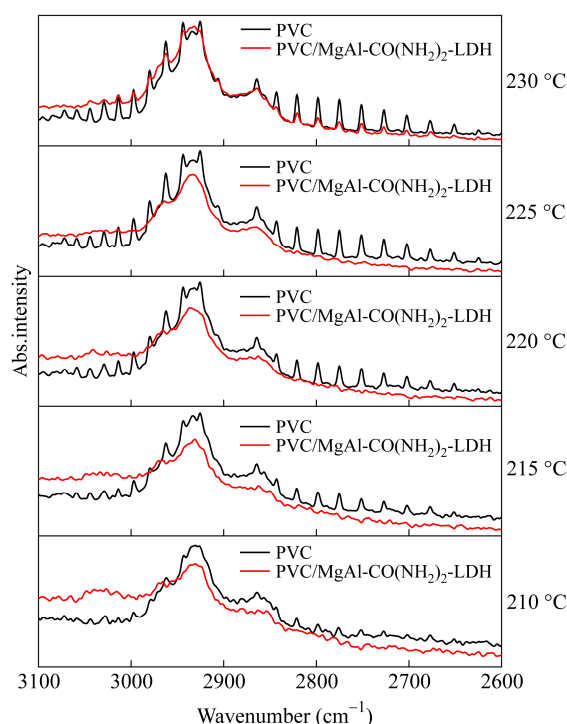


**Fig. 10** FTIR spectra of the evolved gas of PVC at different temperatures

## CONCLUSIONS

In summary, MgAl-LDH (layered double hydroxides) were prepared with  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  by co-precipitation method under constant pH, respectively. The results showed that the LDHs had a layered structure. The PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH composites showed the best thermal stability by thermal aging testing. The compatibility of PVC and LDHs can greatly affect the thermal stability of PVC during the pyrolysis processes. PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH composites exhibit obviously the enhancement of the onset decomposition temperature, the temperature at the maximum rate, and the residue yields during thermal degradation in nitrogen. The results showed PVC/MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH could adsorb HCl, and it's well known that HCl has catalysis effect on degradation of PVC, so MgAl- $\text{CO}(\text{NH}_2)_2$ -LDH could improve thermal stability for PVC. This is important for engineering plastics applications requiring materials to maintain long-term resistance for aging.

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