

Preparation of MgAl LDHs Intercalated with Amines and Effect on Thermal Behavior for Poly(vinyl chloride)

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Abstract

MgAl LDHs intercalated with $\text{CO}(\text{NH}_2)_2$, NH_4Cl and $\text{NH}_3\cdot\text{H}_2\text{O}$ were prepared by co-precipitation and XRD, FT-IR, TGA-DTA and SEM techniques were employed for characterization. The results indicated that the layer-layer spacing of LDHs was enlarged by 0.169, 0.285 and 0.227 Å with the intercalation of $\text{CO}(\text{NH}_2)_2$, NH_4^+ and NH_3 , separately. The effects on thermal stability and degradation behavior of synthesized LDHs where mole ratios of $\text{Mg}/\text{Al}/\text{urea} = 3:1:1$, $\text{Mg}/\text{Al}/\text{NH}_4\text{Cl} = 3:1:1.5$ and $\text{Mg}/\text{Al}/\text{NH}_3\cdot\text{H}_2\text{O} = 3:1:0.5$ were investigated by Congo Red Method and thermogravimetric analysis (TGA) from 25°C - 800°C under N_2 . The TGA and DTA results showed, by incorporating 5% MgAl- $\text{CO}(\text{NH}_2)_2$ LDH, the dehydrochlorination temperature of PVC composites is 12°C higher than MgAl- NH_4^+ and MgAl- NH_3 LDHs. MgAl- NH_3 LDH enhances the ending temperature of the first degradation stage of PVC composites by 8°C compared with MgAl LDH. The LDH intercalated with $\text{CO}(\text{NH}_2)_2$ is proved to be an effective thermal stabilizer for PVC processing.

Keywords

Poly(vinyl chloride), Layered Double Hydroxide, Thermal Stability

1. Introduction

Poly(vinyl chloride) is one of the most widely used commercial thermoplastics, which has many merits such as low cost, good mechanical properties, excellent processing properties. Chlorine builds up 56.8% of PVC, making it to be inherently flam-retardant but meanwhile thermally and photo chemically [1].

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“Unstable structure” such as allyl chloride existed in PVC results in taking off HCl when it is processed, which causes the polymer degradation [2]. Cl^- can be absorbed into the interlayer of LDHs (Layered Double Hydroxides, abbreviated as LDHs), which suppresses the catalysis of the free HCl for the PVC decomposition and improves thermal stability of PVC. Hydrotalcite is a synthetic anionic inorganic laminar compound, which is generally composed of at least two kinds of metal hydroxides [3]. As a kind of “green” inorganic materials with special properties, LDHs can be widely used in adsorption, catalysis and PVC thermal stabilizers, flame retardant, acid scavengers [4]-[10]. The general formula of the chemical composition for LDHs is: $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent metal cation, M^{3+} is a trivalent metal cation, A^{n-} is an interlayered n-valent inorganic (organic) anion [11] [12]. When x is between 0.20 and 0.33, *i.e.* the molar ratio of $\text{M}^{2+}/\text{M}^{3+}$ ranged from 2 to 4 [13]. Great amount of crystal water and absorbed water is present in the structure of hydrotalcite and large quantity of non-bridging hydroxyl and carbonate exists in the interlayer.

In order to improve the thermal stability and compatibility of hydrotalcites for PVC, LDHs must be modified. Ammonia and amines are often used to eliminate odors resulted from the thermal stabilizers such as mercaptan tin used in PVC. Ammonium ion which is obviously alkaline or ammonium ion-containing substituent supplant can be adsorbed on the surface or intercalated between the layers of LDHs. They can strengthen the capacity of absorbing Cl^- ; the steric hindrance between the particles was enhanced, which prevented overlapping between the particles. Abir, S. and his coworkers studied cyanoguanidine-metal and urea-metal complex on the thermal stability for PVC and found out that urea had a thermal stability effect for PVC; urea/organotin mercaptide complex exhibited better stability than mercaptan tin [14]. Hong Zhu developed MgAl-CO_3^{2-} -Cu LDHs with urea as a donor of CO_3^{2-} and studied its thermal stability and smoke suppression; they found out that MgAl-CO_3^{2-} -Cu LDHs had an excellent thermal stability for PVC. Xiaopeng Xu *et al.* investigated kinds of the stability effects of uracil derivatives for PVC and revealed the synergistic effect between Zinc St_2 and n-monomethyl-6-aminothiouracil [15]. Conglin Wang and his coworkers reported the new synthesis routes of MgAlZn-CO_3 LDHs with urea as donor of CO_3^{2-} [16]. Lin Yanjun and his coworkers concerned deeply about the study of MgAl-CO_3 -LDHs and ZnAl-CO_3 LDHs [17] [18].

In this research, $\text{MgAl-NH}_3\cdot\text{H}_2\text{O}$, MgAl-NH_4^+ and $\text{MgAl-CO}(\text{NH}_2)_2$ LDHs nanoparticles with molar ratio of $\text{M}^{2+}/\text{M}^{3+} = 3$ and different molar ratio of Al/amines were synthesized using modified homogeneous co-precipitation method. The thermal stabilizing effects on PVC were studied with Congo red test and TGA/DTA analysis. The structural evolution of LDHs was examined and the influence on improving the thermal stability of PVC was discussed.

2. Experimental

2.1. Synthesis of LDHs

Magnesium nitrate, aluminum nitrate, sodium hydroxide, anhydrous sodium carbonate, $\text{CO}(\text{NH}_2)_2$, $\text{NH}_3\cdot\text{H}_2\text{O}$, NH_4Cl , di-n-octyl phthalate (DOP), all were of analytical grade, provided by the Shanghai Pharmaceutical Group Co., Ltd.; PVC resin, provided by Shanghai Chlor-Alkali Co., Ltd.

LDHs were synthesized by co-precipitation method [19]. LDHs with $\text{Mg}^{2+}/\text{Al}^{3+} = 3$ and different molar ratio of $\text{Al}^{3+}/\text{CO}(\text{NH}_2)_2$, NH_4^+ or NH_3 were dissolved with deionized water as acid solution, separately. Sodium carbonate/sodium hydroxide = 1.6 were formulated into alkaline solution with deionized water. The two solutions were simultaneously added dropwise slowly into the flask (stirring vigorously) which contained 50 ml deionized water at 90°C and the pH is controlled at 9 - 10. After the dropping, kept stirring for another 2 - 3 h with 400 r/min stirring speed. Then the reaction solution was aged at 65°C for 18 h, filtered with de-ionized water to neutrality and then dried in vacuum at 80°C for 15 h. The white solids obtained were ground into a fine powder.

2.2. Characterization

Congo Red tests were employed to examine a static thermal stability of PVC/LDHs composites with 100 phr of PVC, 5 phr of DOP, and 5 phr of synthesized LDHs. According to the standard of ISO 182/1-1990, the time of color change to pH = 3 on Congo Red paper due to the reaction with the released HCl was determined at $190^\circ\text{C} \pm 2^\circ\text{C}$.

Simultaneous thermogravimetric (TGA) and differential thermal analyses (DTA) of PVC/LDHs composites were carried out on a S I I Nano TGA-DTA instrument. Analysis was done from 20°C to 800°C at a heating rate

of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen ($50\text{ mL}\cdot\text{min}^{-1}$) for thermal stability analysis.

X-ray diffraction (XRD) patterns of the LDHs were obtained with a PANalytical X Per X Per P PRO diffractometer using Cu $K\alpha$ radiation with 30 mA and 40 kV power supply. The patterns were recorded over 2θ angles ranging from 5° to 80° , 2θ rate 40 min^{-1} .

Infrared (IR) spectroscopy was recorded using a Nicolet AVATAR 370. Fourier Transform Infrared Spectrometer in the range $4000 - 400\text{ cm}^{-1}$ in tablets in air. The sample were mixed in 0.200 g KBr (p.a.) and used to form tablets with surface of 1 cm^2 .

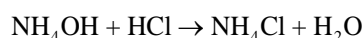
The morphologies were acquired on a S-3400N scanning electron microscope (SEM) manufactured by Japan's Hitachi company.

3. Results and Discussion

3.1. Congo Red Tests

PVC composites with 5 wt% MgAl, MgAl-CO(NH₂)₂, MgAl-NH₄⁺ and MgAl-NH₃ LDHs were prepared by melt blending and the results of Congo Red tests are as shown in **Table 1**. MgAl-CO(NH₂)₂ LDH (1), MgAl-NH₄⁺ LDH (7) and MgAl-NH₃ LDH (10) which have the longest thermal stability time were chosen as the thermal stabilizers to PVC composites in this paper.

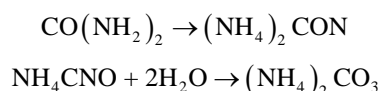
The influence of the LDHs on the thermal stability and dehydrochlorination process of PVC showed that the thermal stability time of neat PVC with 5% MgAl LDHs is only about 18.5 min. After incorporating 5 wt% MgAl-CO(NH₂)₂ (Mg:Al:CO(NH₂)₂ = 3:1:1), MgAl-NH₄⁺ (Mg:Al: NH₄⁺ = 3:1:1.5) and MgAl-NH₃ (Mg:Al:NH₃ = 3:1:0.5) LDHs, separately, the thermal stability time of PVC composites significantly increased to 31.5 min, 38 min and 43 min. The incorporation of NH₃·H₂O(NH₄OH) into LDH platelets significantly increases the thermal stability time of PVC/LDHs composites by more than 20 min longer compared with MgAl LDH. This is because NH₄OH can react with HCl effectively and decrease the catalytic effect of HCl to PVC degradation. The reaction process is as below:



According to literature [20], urea is a very weak Bronsted base ($\text{pK}_b = 13.8$), highly soluble in water, and its hydrolysis rate may be easily controlled by controlling the temperature of the reaction. Urea is easy to form ammonium cyanate and then hydrolyzes into (NH₄)₂CO₃ [21].

Table 1. The results of thermal stability time.

Sample code	Molar ratio	Stability time/min
0	Mg/Al = 3:1	18.5
1	Mg/Al/urea = 3:1:1	31.5
2	Mg/Al/urea = 3:1:0.5	26.0
3	Mg/Al/urea = 3:1:1.5	24.0
4	Mg/Al/urea = 3:1:2	25.5
5	Mg/Al/NH ₄ Cl = 3:1:1	28.5
6	Mg/Al/NH ₄ Cl = 3:1:0.5	30.0
7	Mg/Al/NH ₄ Cl = 3:1:1.5	38.0
8	Mg/Al/NH ₄ Cl = 3:1:2	33.0
9	Mg/Al/ammonia = 3:1:1	30.0
10	Mg/Al/ammonia = 3:1:0.5	43.0
11	Mg/Al/ammonia = 3:1:1.5	39.0
12	Mg/Al/ammonia = 3:1:2	31.0



MgAl-CO(NH₂)₂ LDH can improve the thermal stability by increasing the carbonate ion concentration in the interlayer of LDHs, which will escape from the interlayer over 200 °C and react with HCl. NH₄⁺ will locate on the layer of LDH. However, When NH₄Cl is inserted in the LDHs, NH₄⁺ will locate on the layers and Cl⁻ is in the interlayers. NH₄⁺ can react with HCl as well.

3.2. Powder X-Ray Diffraction

XRD spectra of the samples are shown in **Figure 1**.

Figure 1 shows the MgAl-CO(NH₂)₂, MgAl-NH₄⁺ and MgAl-NH₃ LDHs have low and stable baseline in XRD spectra with sharp absorption peaks for the (003), (006), (110) and (113) planes and broad asymmetric peaks for the (102), (105) and (108) planes which are characteristic of MgAl LDH structure [21]. The shapes of diffraction peaks of MgAl LDH and MgAl-NH₃ LDH are sharp and narrow as well as symmetrical, which demonstrate the crystallization of these two LDHs are complete and the crystal phases are single. The diffraction peaks of MgAl-NH₄⁺ and MgAl-CO(NH₂)₂ LDH became wider and lower, which means their crystallizations are decrease. The Debye-Scherrer formula ($t = 0.9\lambda/\beta\cos\theta_B$), where λ is the wavelength of the radiation used, β is the integral breadth of the peak and θ_B is the Bragg diffraction angle, was employed to calculate the particle sizes of the samples according to the parameters of (003) and (110) planes [22], which are shown in **Table 2**.

The results show that the particle sizes of MgAl LDHs became smaller after being intercalated with CO(NH₂)₂, NH₄Cl and NH₃, that of MgAl-CO(NH₂)₂ is the smallest. This is due to the molecular weight and particles' radius of urea is larger than NH₄Cl and ammonia, with the increase of the molecular weight and particles' radius, intercalation effect becomes worse. At the same time, the crystallines fall down.

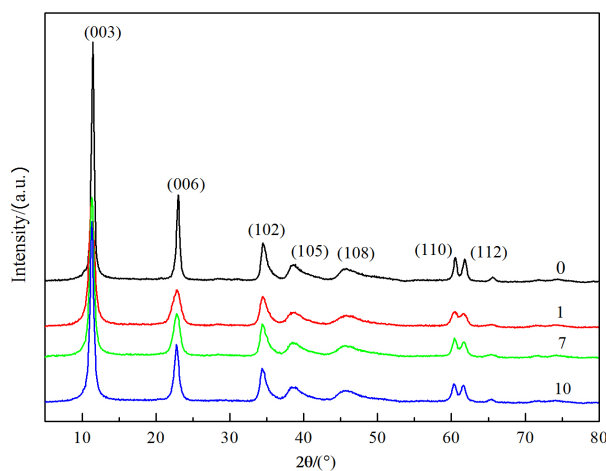


Figure 1. XRD patterns. 0: MgAl LDH; 1: MgAl-CO(NH₂)₂ LDH; 7: MgAl-NH₄⁺ LDH; 10: MgAl-NH₃ LDH.

Table 2. The mass loss rates and the decomposition temperatures.

LDHs samples	The first mass loss stage			
	Temperatures at the beginning (°C)	Temperatures at the max rate (°C)	Temperatures at the end (°C)	Mass loss rate (%)
Mg-Al	259.30	310.69	368.02	57.57
Mg-Al-CO(NH ₂) ₂	278.59	313.41	369.72	56.52
Mg-Al-NH ₄ ⁺	266.14	313.65	367.41	55.14
Mg-Al-NH ₃	266.63	315.61	374.86	54.71

3.3. Infrared Spectroscopy

The information about interlayer anions, crystalline water and the lattice oxygen vibrations in the layer of LDHs can be obtained from the FT-IR analysis. IR spectra of the samples were shown in **Figure 2**.

FT-IR spectra display the characteristic bands for OH and CO bonds that are abundantly present in MgAl-LDH [23]. A broad band is visible ($3436 - 3487 \text{ cm}^{-1}$) that may be attributed to stretching vibrations of the hydroxyl ions and hydroxyl groups of the intercalated water. The weak band at 1620 cm^{-1} is due to the bending mode of water molecules. Compared to MgAl LDH, that of MgAl-CO(NH₂)₂, MgAl-NH₄⁺ and MgAl-NH₃ LDH becomes wider obviously, which results from the stretching vibrations of amino group bonded with hydroxyl and carbonyl. Acromion arose at $2750 - 3050 \text{ cm}^{-1}$, which can be assigned to H₂O-CO₃²⁻ bridge vibration mode formed by hydrogen bonds between water molecules and interlaminar CO₃²⁻ group. Weak peak at $2250 - 2450 \text{ cm}^{-1}$ belongs to the stretching vibration of NH bond. The peak at $1360 - 1380 \text{ cm}^{-1}$ is caused by the asymmetric stretching vibration of C-O bond of CO₃²⁻ group, compared with CO₃²⁻ group in free state (1415 cm^{-1}), this peak obviously shift to lower wavenumber, which indicates CO₃²⁻ inserted between layers not truly free ions and have strong hydrogen bonds with interlaminar water molecules. The peak in MgAl-CO(NH₂)₂ is a little stronger due to the greater concentration of carbonate. While other absorption bands below 800 cm^{-1} are associated with the stretching and bending modes of metal-oxygen bonds [23]. The results proved CO(NH₂)₂, NH₄⁺ and NH₃ inserted into the LDH layer successfully.

3.4. SEM Analysis

The particle morphologies of all of the synthesized materials are investigated by means of SEM, which are shown in **Figure 3**. Pure MgAl LDH shows a clear and structured crystalline perfection (**Figure 4(0)**) and the lamellae crystals distribute on the particles. MgAl-CO(NH₂) and MgAl-NH₃ LDHs exhibit layer structures and the crystals dispersed on the surface of the particles, but the crystal sizes are smaller and agglomerate into a big block (**Figure 4(1)** and **Figure 4(10)**). Sample 7 doesn't have obvious crystal structures and the slice groups tend to move together. It can clearly be seen that intercalating ammonium and urea weaken the grain dispersion and the particle sizes became larger, the layer spacing became larger, the surface area becomes larger and had the tendency to agglomerate. The SEM analysis further validated the effect of ammonium and urea to the crystal structures of LDHs.

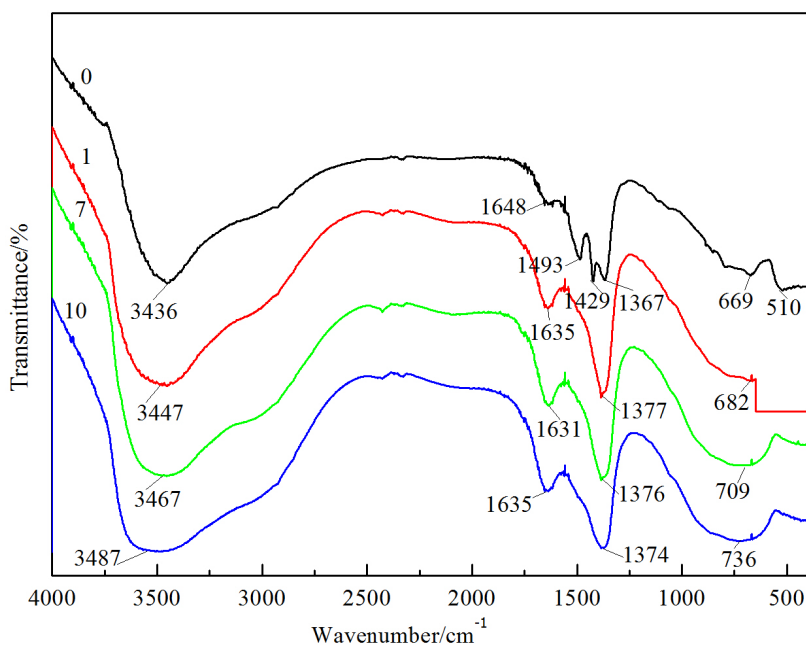


Figure 2. IR spectra. 0: MgAl LDH; 1: MgAl-CO(NH₂)₂ LDH; 7: MgAl-NH₄⁺ LDH; 10: MgAl-NH₃ LDH.

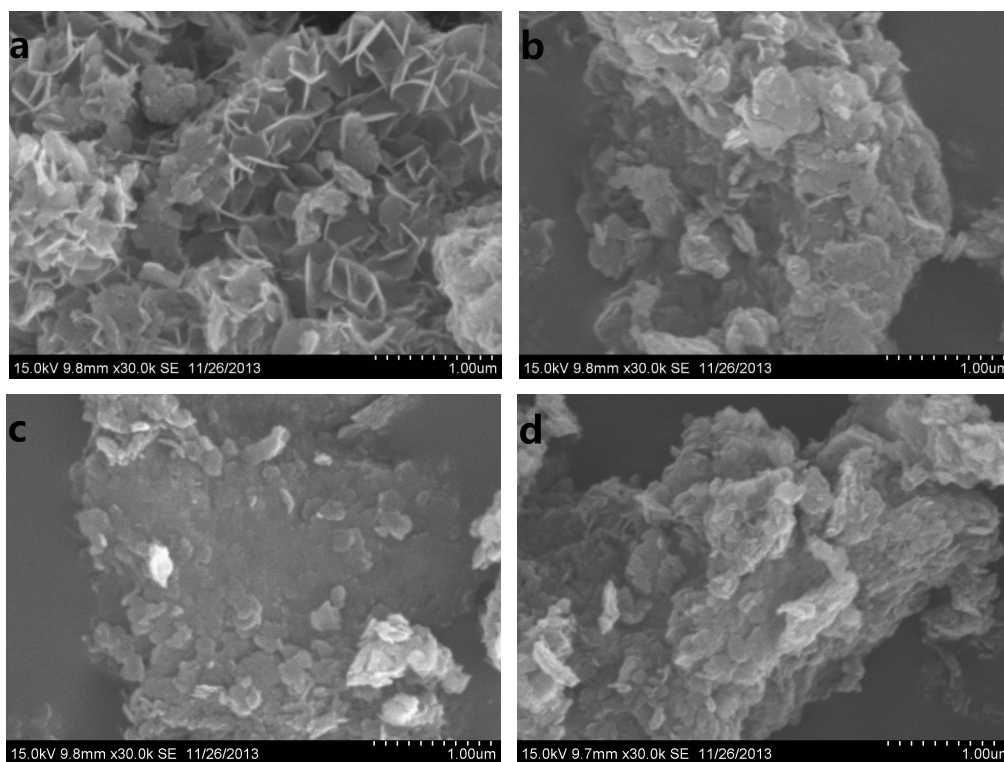


Figure 3. SEM images. (a) MgAl LDH; (b) MgAl-CO(NH₂)₂ LDH; (c) MgAl- NH₄⁺ LDH; (d) MgAl-NH₃ LDH.

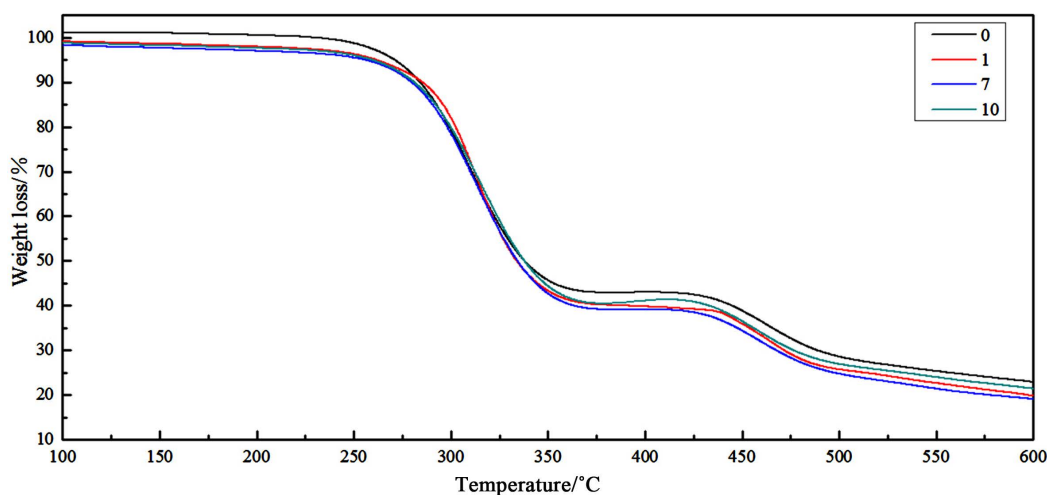


Figure 4. TGA curves. 0: MgAl LDH; 1: MgAl-CO(NH₂)₂ LDH; 7: MgAl- NH₄⁺ LDH; 10: MgAl-NH₃ LDH.

3.5. Thermal Stability Analysis

TGA and DTA curves in N₂ for PVC composites with four kinds of LDHs are shown in **Figure 4** and **Figure 5** and the analysis data were listed in **Table 2**. The degradation of PVC resin usually consists of two steps. The initial step is the dehydrochlorination which includes autocatalysis process by releasing HCl and the formation of conjugated polyene sequences. The second step is the decomposition of polyene back ones and formation of residual chars [24]. The TG curves may be divided into two well-differentiated main regions. In the first one, ranging from 80°C to 400°C, there is a broad endothermic peak in DTA related to the dehydrochlorination and the formation of conjugated polyene sequences. The released HCl will catalytically speed up the degradation of

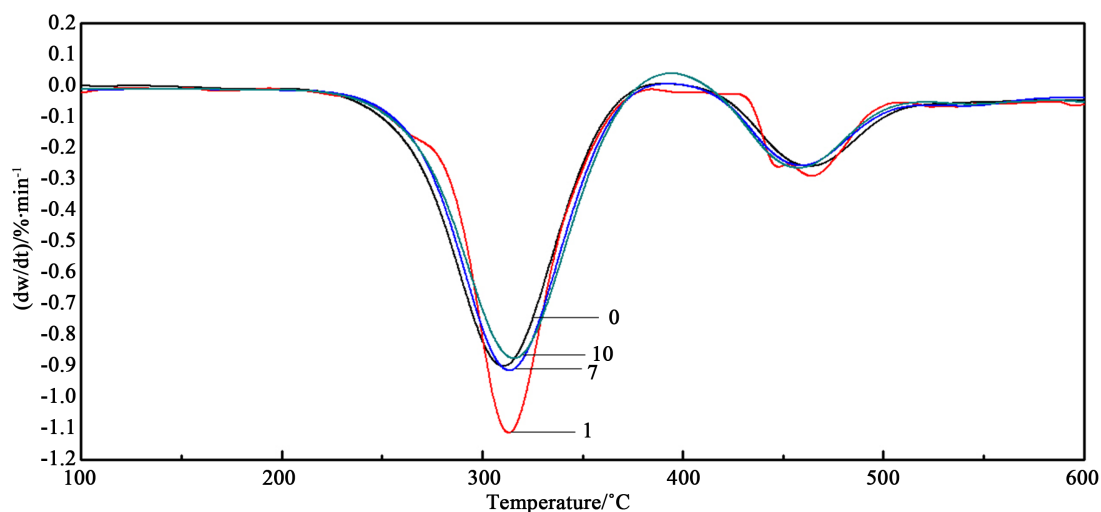


Figure 5. DTG curves. 0: MgAl LDH; 1: MgAl-CO(NH₂)₂ LDH; 7: MgAl-NH₄⁺ LDH; 10: MgAl-NH₃ LDH.

PVC. The hydroxyl groups, as well as the CO₃²⁻ and other interlayer anions such as ammonia removal from the in the brucite-like layers of hydrotalcites in this temperature range can react with hydrochlorination and restrain PVC degradation further effectively [24]. The second region ranging over 400°C, another small endothermic peak attribute to decomposition of polyene backbones and formation of residual chars. The first step can be used to describe the degradation of the processing and use for PVC.

As for PVC/MgAl LDHs, the first stage of weight loss begins as early as 259.30°C and reaches the maximum rate at 310.69°C, and then ends at 368.02°C. While the initial degradation temperatures of PVC/MgAl-CO(NH₂)₂, MgAl-NH₄⁺ and MgAl-NH₃ LDHs are 278.59°C, 266.14°C and 266.63°C, separately. The results prove that the addition of MgAl-CO(NH₂)₂ LDH increases the temperature by 20°C, which is about 7°C by MgAl-NH₄⁺ and MgAl-NH₃ LDHs. At the beginning of PVC degradation, the catalytic action of HCl released from PVC chain is the key. The best thermal stability of MgAl-CO(NH₂)₂ LDH may be assigned to the increase of carbonate ion concentration in the interlayers of LDHs which can react more HCl. The increase of thermal stability resulted from adding MgAl-NH₄⁺ and MgAl-NH₃ LDHs can be attributed to NH₄⁺ and NH₃ can also react with Cl⁻ bonded in the interlayers through anion exchange except OH⁻ and CO₃²⁻. As for PVC, thermal stabilizers play an important role during the processing ranging from 100°C to 250°C, therefore, we can conclude MgAl-CO(NH₂)₂ is a kind of effective thermal stabilizers for PVC processing.

With the temperature rises up over 300°C, PVC composites reach the maximum degradation rate and small molecules and ions in the interlayer escape continuously and polyene backbones formed. Chloride ions begin to react with metal ions into lewis acid, which act as reductive crosslinking agent and suppress benzene production. It can be seen from **Table 2**, at the end of the first step, the weight loss of PVC/MgAl-NH₃ LDH composite ends at 374.86°C, which is higher than the other three composites by 5°C - 7°C. It is because its molecule weight is smaller, the concentration of magnesium and aluminum ions which act as reductive crosslinking agent are higher in contrast, so more crosslinking structures can be formed to suppress benzene production. This result is consistent with that of Congo Red tests and indicated the better long term thermal stability of MgAl-NH₃ LDH.

4. Conclusions

MgAl LDHs intercalated with CO(NH₂)₂, NH₄⁺ and NH₃ have been prepared by co-precipitation method. XRD and FT-IR analysis proved that the synthesized LDHs have the characterized diffraction peaks and functional groups, while their crystalline declined. WAXS studies have enabled a detailed description of the layer-layer spacing to increase 0.169, 0.285 and 0.227 Å. The change of the interlamellar distance is ascribed to the CO₃²⁻, NH₄⁺ and NH₃ intercalating into the MgAl-CO(NH₂)₂ LDH, MgAl-NH₄⁺ LDH and MgAl-NH₃ LDH through the anion exchange.

The addition of MgAl-CO(NH₂)₂ LDH into PVC matrix significantly increases the dehydrochlorination tem-

perature, and the addition of MgAl-NH₃ increases the long term thermal stability for PVC. When compared with MgAl LDH, MgAl-CO(NH₂)₂ LDH enhances the initial degradation temperature of PVC composites by about 20°C, while MgAl-NH₃ LDH enhances the temperature of 5°C - 7°C at the end of the first degradation stage.

These results confirm that MgAl-CO(NH₂)₂ LDH can restrain PVC degradation effectively during its processing, and MgAl-NH₃ LDH is a good kind of long term thermal stabilizer.

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