

# Effects of Copper-Containing Layered Double Hydroxide on Thermal and Smoke Behavior of Poly(vinyl chloride)

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**ABSTRACT:** Thermal and smoke properties of poly(vinyl chloride)/copper-containing layered double hydroxide (MgCuAl-LDH) composites were studied in this article. Highly crystallized LDH with platelet size at micrometer scale was prepared via urea hydrolysis and further intercalated with a variety of anions. X-ray diffraction results indicated an enlargement of basal spacing to 2.54 nm for dodecylsulfonate-intercalated LDH. The effects of LDHs on thermal stability and degradation behavior of PVC were investigated by Congo Red tests and thermogravimetric analysis (TGA). By incorporating 3 wt % LDHs, the thermal stability times of carbonated MgAl-LDH and

MgCuAl-LDH/PVC composites were even three and five times of that of neat PVC. The TGA showed an increase of polyene sequences and char residues formed during PVC pyrolysis. MgCuAl-LDH/PVC composites gave the best reduction in maximum density of smoke, i.e., 25% lower than that of MgAl-LDH/PVC composites. However, the organomodification of LDH by anion exchange gave no contribution to improvement of thermal stability of PVC. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 273–281, 2011

**Key words:** poly(vinyl chloride); layered double hydroxides; degradation; thermal properties; smoke density

## INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used commercial thermoplastics. It has many merits such as low cost, good mechanical properties, excellent processability, and so on. Chlorine builds up 56.8% of PVC, making it to be inherent flame-retardant but meanwhile thermally and photochemically unstable. Various kinds of additives should be added during processing to reduce its decomposition or to enhance the other properties. Recently, two conceptions about designing next generation “green” additives have been widely accepted. The first is that layered double hydroxides (LDHs) could enhance thermal stability of PVC efficiently.<sup>1–5</sup> The second is that copper compounds might be the most effective smoke suppressants for PVC.<sup>6–10</sup> Therefore, it is interesting to investigate how the combination of the two conceptions, which means the synthesis

of copper-containing LDHs, will actually affect the thermal behavior of PVC.

LDHs are a group of brucite-like layered materials, which contain exchangeable interlayer anions and mixed metal hydroxide layers. The general formula of LDHs is  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-x/n}yH_2O]^{x-}$ , where  $M^{II}$  is a divalent metal cation ( $M^{II}$ : Mg, Zn, Ni, Co, etc.),  $M^{III}$  is a trivalent metal cation ( $M^{III}$ : Al, Fe, etc.), and A stands for  $n$  valence inorganic or organic acid anions.<sup>11</sup> It is discovered that LDHs could be effective flame retardant for most polymers, leading to significant reduction in peak heat release rate (PHRR). Qu's group initially fabricated exfoliated LDHs/polymer nanocomposites with enhanced thermal stability and fire performance,<sup>12–16</sup> while works by Wilkie and coworkers' group systematically investigated the effect of LDHs with various interlayer anions on flame retardancy of different types of polymer matrices,<sup>17–25</sup> both polar and nonpolar polymers. Their great works contributed to a better understanding of the mechanisms that how LDHs affect the flame retardancy of polymer/LDH composites. Besides, novel strategies for fabricating flame retardant polymer/LDH nanocomposites have been developed, e.g., synergistic effect of LDHs and phosphate compounds,<sup>26</sup> borate,<sup>27</sup> intumescent flame retardants,<sup>28</sup> and metal oxides.<sup>29</sup> LDHs also have considerable HCl absorption capacity and could be used as thermal stabilizer of PVC. The adsorption of HCl proceeds by a two-step process. First, LDHs

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absorb HCl through interlayer anion exchange to inhibit the autocatalytic degradation of PVC.<sup>30</sup> Then, LDH layers react with HCl to form metal chlorides with total destruction of LDH structures.<sup>31</sup> Lin et al.<sup>1</sup> reported that MgAl-CO<sub>3</sub>-LDH with Mg/Al ratio of 2 has the best thermal stabilizing effect and the interlayer carbonate ions are more important in stabilizing PVC against thermal degradation than the overall HCl adsorption capacity. Xu et al.<sup>3</sup> found that Zn<sub>2</sub>Al-CO<sub>3</sub>-LDH could facilitate dehydrochlorination at lower temperature. Recently, PVC/LDH composites prepared by *in situ* polymerization<sup>4</sup> and solution blending<sup>5</sup> were reported to increase both thermal stability time and dehydrochlorination temperature.

It is found that copper compounds might be the most effective class of smoke suppressants for PVC and the mechanism of reductive coupling had been given and identified in experiments.<sup>6</sup> Li investigated the flame retardancy and smoke suppression behavior of PVC/metal oxide composites by cone calorimeter, and it was found that copper-containing formulae is the most efficient.<sup>7,8</sup> Efforts have been made to incorporate copper compounds into traditional smoke suppression agents to form synergetic effect.<sup>9</sup> However, such agents had poor compatibility with PVC and deteriorated the mechanical properties of PVC products. A new carrier for copper is therefore required to be used as smoke suppressant for PVC or other polymer matrices.

In this study, novel copper-containing LDHs with large platelets in micrometers were prepared via urea hydrolysis method.<sup>32</sup> LDHs as a carrier for copper ions could form a new class of environmental friendly thermal stabilizers with efficient smoke suppression effect and mechanical enhancement. Thermal and smoke behavior of 3 wt % copper-containing LDH/PVC composites was examined by Congo Red tests, thermogravimetric analysis (TGA) and specific optical density of smoke tests. Anion exchange of LDHs and their effects on the decomposition of PVC were also discussed.

## EXPERIMENTAL

### Sample preparation

The reagents used here [MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, urea, NaNO<sub>3</sub>, NaCl, and sodium dodecylsulfonate (SDS)] were of analytical grade, purchased from Sinopharm Chemical Reagent, China. PVC resin used was SG-5 with average polymerization degree of 1000–1100. The dibasic lead phosphate used as PVC thermal stabilizer was of industrial grade.

### Synthesis of MgAl-CO<sub>3</sub>-LDH and copper-containing LDH

MgAl-CO<sub>3</sub>-LDH was synthesized by urea hydrolysis method as described by Costantino et al.<sup>32</sup> In a typi-

cal procedure, MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O and urea were dissolved in deionized water with the molar ratios of Al<sup>3+</sup>/(Mg<sup>2+</sup>+Al<sup>3+</sup>) and urea/(Mg<sup>2+</sup>+Al<sup>3+</sup>) equal to 0.33 and 3.3, respectively. The final metal concentration of the solution was fixed to be 0.05M. The mixed solution was then transferred into a 500 mL flask equipped with a reflux condenser, and vigorously stirred at 90°C for 48 h. The resulting white precipitate was filtered, washed with deionized water and ethanol for several times, and dried at room temperature to obtain MgAl-CO<sub>3</sub>-LDH powder.

Similarly, for the synthesis of copper-containing LDH, CuCl<sub>2</sub>·2H<sub>2</sub>O was introduced to replace 1/4 molar of MgCl<sub>2</sub>·6H<sub>2</sub>O, forming a blue solution with the molar ratios of Cu<sup>2+</sup>/Mg<sup>2+</sup> of 0.33, Al<sup>3+</sup>/total metal concentration of 0.33 and urea/total metal concentration of 3.3. Again, the total metal concentration was fixed to be 0.05M. The rest of the procedures were the same as the synthesis of MgAl-CO<sub>3</sub>-LDH. Finally, pale-blue powder of MgCuAl-CO<sub>3</sub>-LDH was obtained.

### Decarbonation and anion exchange of copper-containing LDH

The decarbonation of CO<sub>3</sub>-LDHs was conducted as described.<sup>33</sup> Typically, 0.5 g CO<sub>3</sub>-LDH was added into 500 mL NaCl-HCl mixed solution (concentration: 1M for NaCl and 3.3 mM for HCl). After purging with N<sub>2</sub>, the vessel was sealed and continuously stirred for 24 h at ambient temperature. The resulting suspension was filtered as described above.

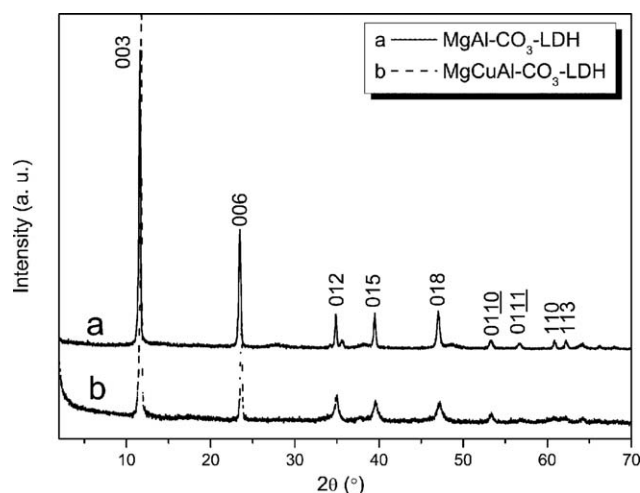
The LDHs with various kinds of interlayer anions were prepared through a further anion exchange process using the obtained Cl-LDH as precursor. For NO<sub>3</sub>-LDH [or dodecylsulfonate (DS)-LDH], 0.5 g as-obtained Cl-LDH was dispersed into 500 mL 0.1M NaNO<sub>3</sub> (or SDS) solution, purged with N<sub>2</sub> and stirred for 24 h. The same procedure was employed as described above.

### Preparation of PVC/LDH composite samples

PVC/LDH composites were prepared by melt blending. A total of 58.2 g PVC and 1.8 g corresponding LDHs (or other PVC thermal stabilizer) were added into a 60 cm<sup>3</sup> Brabender batch mixer at 180°C for melt compounding for 5 min with a screw speed of 50 rpm. The as-mixed composites were then made into thin sheets with thickness of 1.0 ± 0.1 mm by compression molding at 180°C.

### Characterization

X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO diffractometer (CuK $\alpha$  radiation,  $\lambda$  = 0.1542 nm). The morphology



**Figure 1** XRD patterns of (a) MgAl-CO<sub>3</sub>-LDH and (b) MgCuAl-CO<sub>3</sub>-LDH.

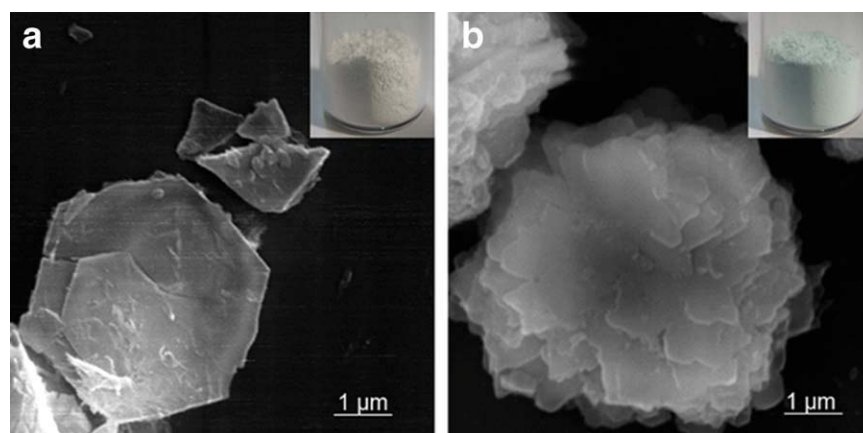
of the as-synthesized LDHs was examined with a Vega TS 5166mm scanning electron microscope (SEM). Transmission electron microscopy (TEM) observations were performed under an acceleration voltage of 200 kV with a JEOL 2100 TEM. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Nexus 470 infrared spectrophotometer using KBr discs, with 64 scans average with scan range of 4000–400 cm<sup>-1</sup> and at a resolution of 4 cm<sup>-1</sup>. TGA was performed from 100 to 600°C at a heating rate of 10°C/min by using a Perkin-Elmer Pyris-1 TGA under nitrogen and air atmosphere. Congo Red tests were employed to examine the early thermal stability of PVC/LDH composites. According to the standard of ISO 182/1–1990, the time of color change on Congo Red paper due to the reaction with the released HCl was determined at 175°C. The specific optical density of smoke generated by the composites was obtained under flaming

mode using a Govmark SD-1 smoke density tester, according to ASTM E662-09.

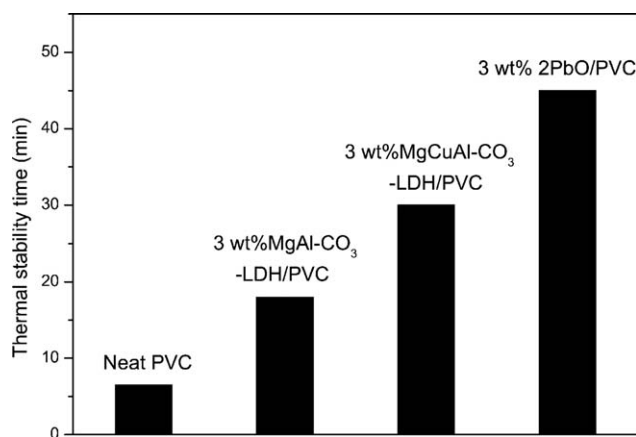
## RESULTS AND DISCUSSION

### Structure of the as-synthesized LDHs

When compared with conventional coprecipitation method, urea hydrolysis method enables “homogeneous precipitation” of metal ions which could aid in the formation of large and highly crystallized LDHs at micrometer scale. Figure 1 shows the XRD patterns of LDHs synthesized by urea hydrolysis. All the diffraction peaks are sharp and narrow, indicating the formation of highly crystalline structure. The (003) diffraction peaks for both MgAl-CO<sub>3</sub>-LDH and MgCuAl-CO<sub>3</sub>-LDH appear at 2θ angles of about 11.7° and their (110) diffraction peak at about 61°. The lattice parameters, *a* and *c*, of MgCuAl-CO<sub>3</sub>-LDH are calculated to be 0.30 nm and 2.26 nm, respectively, which are in good agreement with those of the well-known carbonated LDHs.<sup>1,3,5,33</sup> It is noticed that the (110) plane of MgCuAl-CO<sub>3</sub>-LDH is much weaker and broader than that of MgAl-CO<sub>3</sub>-LDH, which means that the crystallite size in *a* axis for MgCuAl-CO<sub>3</sub>-LDH is smaller than that of MgAl-CO<sub>3</sub>-LDH. It may attribute to the Jahn–Teller effect of Cu<sup>2+</sup> that destroys the well-organized structure of magnesium aluminum hydroxide layer and forms a jagged polygon shape instead of regular hexagon platelets,<sup>34</sup> as confirmed by SEM images for both types of LDHs (Fig. 2). MgAl-CO<sub>3</sub>-LDH sample consists of regular hexagonal platelets with lateral size as large as about 5 μm, while MgCuAl-CO<sub>3</sub>-LDH is observed as stacks of irregular platelets with lateral size of about 7 μm. The insets in Figure 2 are the optical photographs of the powdery samples of the as-synthesized LDHs. MgAl-CO<sub>3</sub>-LDH is white powder



**Figure 2** SEM images of (a) MgAl-CO<sub>3</sub>-LDH and (b) MgCuAl-CO<sub>3</sub>-LDH. The insets are photographs of as-synthesized LDH powder. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** Thermal stability time of neat PVC and its composites containing lead salts, MgAl-CO<sub>3</sub>-LDH and MgCuAl-CO<sub>3</sub>-LDH measured by Congo Red tests.

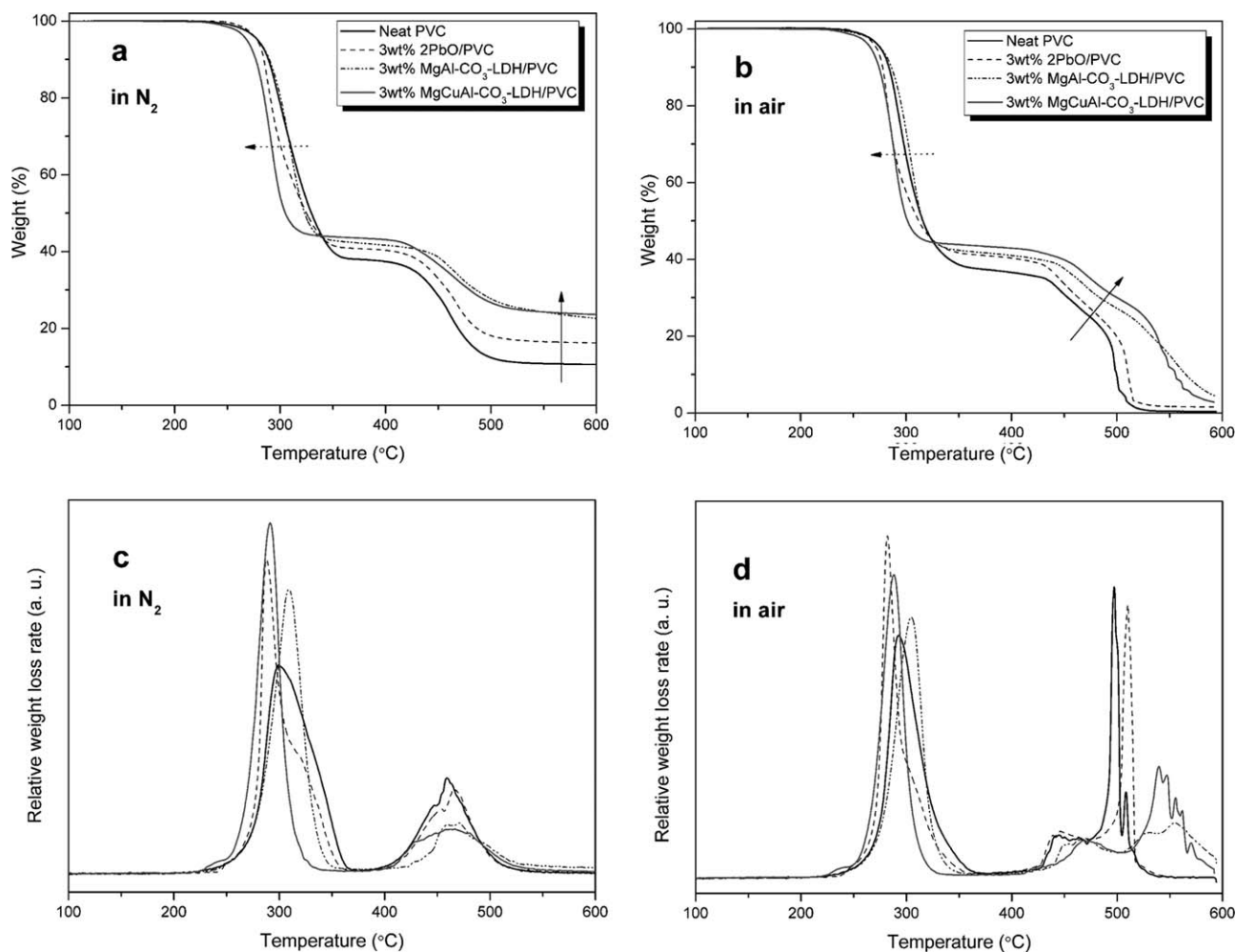
while the color of MgCuAl-LDH turns to pale blue due to the incorporation of copper ions.

#### Effect of carbonated LDHs on thermal stability of PVC

Neat PVC and its composites with 3 wt % MgAl-CO<sub>3</sub>-LDH, 3 wt % MgCuAl-CO<sub>3</sub>-LDH, and 3 wt % dibasic lead phosphate were prepared by melt blending and compression molding. The influence of these additives on the thermal stability and dehydrochlorination process of PVC was investigated by Congo Red tests, as shown in Figure 3. The thermal stability time of neat PVC is only about 6 min. After incorporating 3 wt % carbonated MgAl-LDH, the thermal stability time of PVC is significantly increased to 18 min. Addition of 3% carbonated MgCuAl-LDH leads to more prominent effect, where the thermal stability time is increased to 30 min. While carbonated MgAl-LDH is proven to be an efficient thermal stabilizer for PVC, the incorporation of copper ions into LDH platelets significantly increases the thermal stability time of PVC/carbonated LDH composites by more than 50%. This is because copper ions could act as reductive coupling agent in PVC under pyrolysis condition, thus accelerates the formation of crosslinks from allylic chlorides on adjacent polymer chains.<sup>6</sup> The crosslinked networks could protect the polymer chains against thermal decomposition, even in the dehydrochlorination process. However, comparing with conventional thermal stabilizer such as lead salts, carbonated LDHs are less effective on the improvement of thermal stability of PVC. This is probably due to the huge difference in HCl adsorption capacity between LDHs and basic metal salts.

It is known that the degradation of PVC resin usually consists of two steps.<sup>3,6</sup> The initial step is the dehydrochlorination which includes autocatalysis

process by releasing HCl<sup>30</sup> and the formation of conjugated polyene sequences. The second step is the decomposition of polyene backbones and the formation of residual chars. TGA and DTG curves in N<sub>2</sub> and air atmospheres for PVC composites with different additives are shown in Figure 4. Two major stages of weight loss can be clearly observed. As for neat PVC, the first stage of weight loss begins as early as at 240°C. It reaches the maximum rate at 300°C in N<sub>2</sub> and 293°C in air, respectively, while ends at 365°C in both atmospheres. These results are consistent with the previous report.<sup>3,35</sup> TGA data of neat PVC and its LDH composites are listed in Table I. In the first step, the strong tendency of carbonated LDHs to adsorb HCl facilitates the chlorine atom from leaving PVC backbone, forming chloride intercalated LDHs and further decomposition to corresponding chloride salts. It is reported<sup>36</sup> that chloride salts could promote the dehydrochlorination immediately after initialization, e.g., ZnCl<sub>2</sub>, which catalytically receive chloride ion from PVC to form a carbonium ion. The carbonium ion decomposes to alkene and releases a proton that combines with immediate MCl<sub>x</sub><sup>-</sup> (M = Zn, Al, . . .). Finally, HCl is released and chloride salts are recovered.<sup>36</sup> In this study, we assume that MgCl<sub>2</sub>, CuCl<sub>2</sub>, and AlCl<sub>3</sub>, which are freshly generated by LDHs adsorbing HCl and consequent decomposition, act as Lewis base and catalytically cofacilitate PVC dehydrochlorination. Therefore, the dehydrochlorination temperatures of PVC/carbonated LDH composites are decreased. As it can be seen, by incorporating 3 wt % MgCuAl-CO<sub>3</sub>-LDH into PVC matrix the 10 and 40% weight loss temperature were decreased by 10 and 20°C, respectively. The dehydrochlorination weight loss proves that the addition of LDHs retains more chloride in PVC/LDH mixture than neat PVC, which is about 6% for MgCuAl-CO<sub>3</sub>-LDH and 4% for MgAl-CO<sub>3</sub>-LDH, respectively. These phenomena may be ascribed to two reasons. First, as mentioned above, through anion exchange and further decomposition of LDHs, chloride ions are bonded either in interlayers of LDHs or directly in the form of chloride salts. Moreover, the catalytic crosslinking induced by LDHs may retain more chloride in polyene backbones. In the second step, the scission of polyene sequences by cracking, crosslinking, dehydrocarbonation, and charring leads to residual chars, which could resist high-temperature and mass transfer. LDH layers containing metal ions could act as Lewis acid to induce a cationic crosslinking (Friedel-Craft reaction) between two polyene backbones,<sup>6</sup> while copper could effectively act as reductive crosslinking agent and suppress benzene production. Because of the effect of crosslinking, char residue in N<sub>2</sub> at 600°C for PVC/LDH composites was increased by 122.6% for MgCuAl-CO<sub>3</sub>-LDH and 113.2% for MgAl-CO<sub>3</sub>-LDH.



**Figure 4** TGA and DTG curves of PVC with different additives in  $N_2$  (a,c) and air (b,d) at heating rate of  $10^\circ\text{C}/\text{min}$ .

In air, similar to the case in  $N_2$ , the 70% weight loss temperature was increased by  $50^\circ\text{C}$  for MgCuAl- $\text{CO}_3$ -LDH and  $30^\circ\text{C}$  for MgAl- $\text{CO}_3$ -LDH. Therefore, we can conclude that the thermal stability of polyene sequences increases significantly upon the addition of LDHs in both  $N_2$  and air.

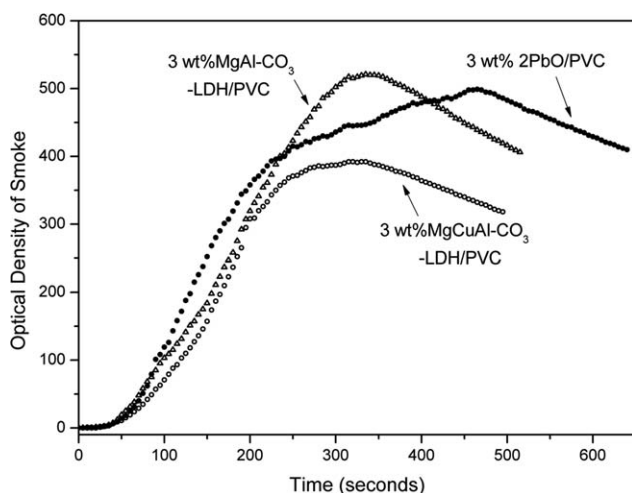
Specific optical density of smoke generated by PVC composites are given in Figure 5. The maximum density of smoke decreases significantly for PVC/MgCuAl-LDH composites, i.e., 25 and 20% lower than those of PVC/MgAl-LDH composites and traditional PVC/lead salts composites, respectively.

**TABLE I**  
Summary of TGA Data for Neat PVC and its Composites in  $N_2$  and Air at Heating Rate of  $10^\circ\text{C}/\text{min}$

	Neat PVC	3 wt % MgAl- $\text{CO}_3$ -LDH/PVC	3 wt % MgCuAl- $\text{CO}_3$ -LDH/PVC	3 wt % 2PbO/PVC
In $N_2$				
$T_{10\%}$ ( $^\circ\text{C}$ ) <sup>a</sup>	289	290	277	285
$T_{40\%}$ ( $^\circ\text{C}$ )	318	314	296	310
Dehydrochlorination (%) <sup>b</sup>	61.9	57.5	55.8	59.1
Char residue yield at $600^\circ\text{C}$ (%)	10.6	22.6	23.6	16.2
In air				
$T_{10\%}$ ( $^\circ\text{C}$ )	284	286	274	278
$T_{40\%}$ ( $^\circ\text{C}$ )	305	308	293	297
Dehydrochlorination (%)	62.4	57.7	55.7	58.5
$T_{70\%}$ ( $^\circ\text{C}$ )	454	484	500	463
Char residue yield at $600^\circ\text{C}$ (%)	0.4	4.3	2.9	1.6

<sup>a</sup>  $T_{10\%}$  is the temperature for 10% weight loss.

<sup>b</sup> Dehydrochlorination (%) is the dehydrochlorination weight loss.



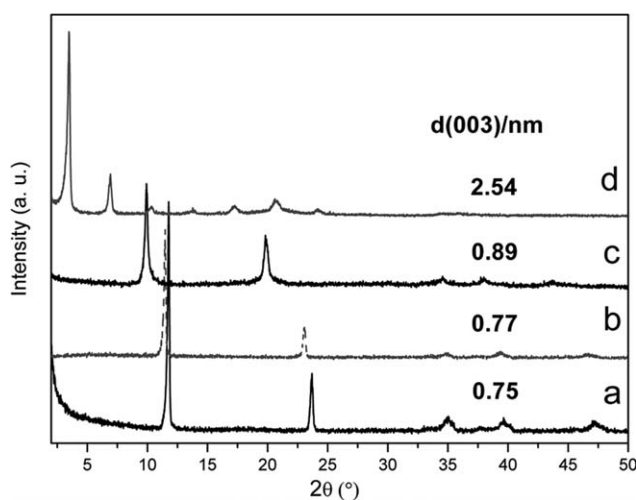
**Figure 5** Specific optical density of smoke generated by PVC composites. (As the density of smoke generated by neat PVC is too high to be measured reliably, the figure of that of neat PVC is not shown.)

As to the case in neat PVC, the density of smoke generated is too high to be measured reliably. In our serial experiments, the results are not satisfying to be presented correctly though it is obvious that the density of smoke is much high than its composites. It is reported that the maximum optical density of neat PVC could reach 800 (under the standard of ASTM E662-95).<sup>37</sup> When taking this value of neat PVC for comparison, the maximum density of smoke significantly decreases by almost 50% for PVC/MgCuAl-LDH composites.

### Anion exchange of MgCuAl-LDH

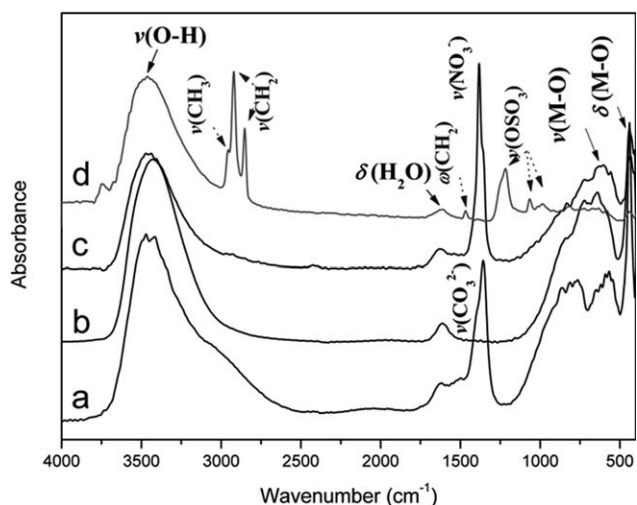
To achieve fine dispersion of LDHs in polymer composites, a suitable organomodification of LDHs is usually necessary. The conventional method for anion exchange and the introduction of long-chain organic anions could effectively expand or swell the interlayer regions. Consequently, intercalated or exfoliated LDH/polymer nanocomposites could be obtained. The decarbonation of the as-synthesized MgCuAl-LDH was conducted using a salt-acid mixing solution according to Iyi et al.<sup>38</sup> XRD patterns of the LDH samples obtained by anion exchange with  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{DS}^-$  interlayer anions are shown in Figure 6. After anion exchange, the basal diffractions with  $d$ -spacing value of 0.75 nm for  $\text{CO}_3^{2-}$ -LDH disappeared, instead, new series of basal reflections at lower  $2\theta$  angles appeared. The basal spacings of LDH samples with  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{DS}^-$  interlayer anions were increased to 0.77, 0.89, and 2.54 nm, respectively.

FTIR spectra also confirm the complete decarbonation and anion exchange, as shown in Figure 7. For all LDHs, the broadband at  $3460\text{ cm}^{-1}$  is assigned to

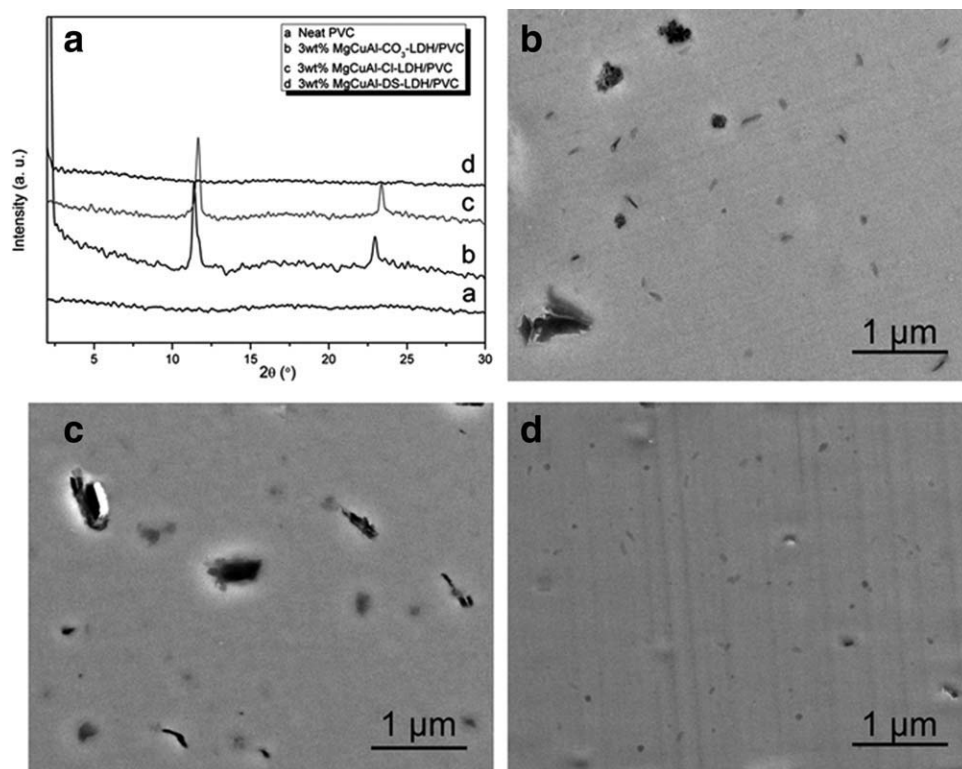


**Figure 6** XRD patterns of MgCuAl-LDH with different interlayer anions: (a)  $\text{CO}_3^{2-}$ , (b)  $\text{Cl}^-$ , (c)  $\text{NO}_3^-$ , and (d)  $\text{DS}^-$ .

the O—H stretching modes of water molecules, which are being trapped within the LDH interlayers. The weak band at  $1620\text{ cm}^{-1}$  is due to the bending mode of water molecules, while other absorption bands below  $800\text{ cm}^{-1}$  are associated with the stretching and bending modes of metal-oxygen bonds. In Figure 7, the strong peak at  $1356\text{ cm}^{-1}$  on curve *a* belongs to the  $\nu_3$  vibration of  $\text{CO}_3^{2-}$  of MgCuAl-LDH intercalated with  $\text{CO}_3^{2-}$ . After anion exchange with NaCl-HCl mixed solution, the disappearance of  $1356\text{ cm}^{-1}$  peak on curve *b* indicates the complete decarbonation by the formation of  $\text{Cl}^-$ -LDH. Further, anion-exchanged samples were prepared by using  $\text{Cl}^-$ -LDH as precursor. The strong absorption peak at  $1384\text{ cm}^{-1}$  of curve *c* in Figure 7 is due to N—O stretching vibration mode of  $\text{NO}_3^-$



**Figure 7** FTIR spectra of MgCuAl-LDH with different interlayer anions: (a)  $\text{CO}_3^{2-}$ , (b)  $\text{Cl}^-$ , (c)  $\text{NO}_3^-$ , and (d)  $\text{DS}^-$ .



**Figure 8** XRD patterns (a) and TEM images of PVC/LDH composites: (b) 3 wt % MgCuAl-CO<sub>3</sub>-LDH/PVC, (c) 3 wt % MgCuAl-Cl-LDH/PVC, and (d) 3 wt % MgCuAl-DS-LDH/PVC.

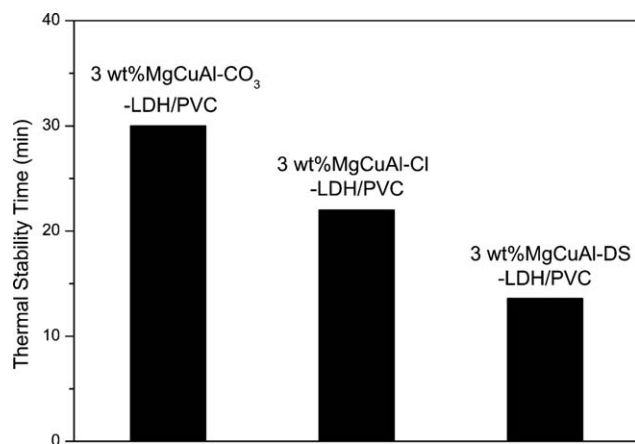
ions. On curve *d* in Figure 7, asymmetric and symmetric CH<sub>2</sub> stretching vibration bands at 2923 and 2853 cm<sup>-1</sup>, stretching vibration of terminal CH<sub>3</sub> group at 2955 cm<sup>-1</sup>, and stretching mode of sulfate in the range of 1300–900 cm<sup>-1</sup> are observed, which coincide with the vibration modes of DS<sup>-</sup>. Therefore, by combining the XRD and FTIR results, it can be concluded that by using the anion exchange process as described above, the decarbonation proceeds completely and the LDH samples with different interlayer anions have been successfully prepared.

#### Effect of the anion-exchanged LDHs on thermal stability of PVC

XRD patterns of (a) neat PVC, (b) PVC/MgCuAl-CO<sub>3</sub>-LDH, (c) PVC/MgCuAl-Cl-LDH, and (d) PVC/MgCuAl-DS-LDH composites (3 wt % of LDHs loaded) are shown in Figure 8a. It can be seen that neat PVC shows no diffraction peaks in the measured 2θ range of 2°–30°. The two diffraction peaks for PVC/MgCuAl-CO<sub>3</sub>-LDH composites at 2θ values of 11.4° and 22.9° refer to (003) and (006) diffractions of Cl-LDH. It can be inferred that during processing, CO<sub>3</sub>-LDH transformed to Cl-LDH via anion exchange with hydrogen chloride. However, when Cl-LDH was added into PVC matrix, Cl-LDH was not intercalated with polymer chains but showed a

slight collapse between LDH galleries. This is indicated by a slight shift of the basal reflection toward higher 2θ angle by about 0.2°. This phenomenon may be attributed to the dissociation of interlayer chloride to participate in the HCl autocatalysis process. As for PVC/MgCuAl-DS-LDH composite, no basal diffraction was observed, suggesting that the organomodified LDH layers are probably exfoliated and homogeneously dispersed in PVC matrix. TEM observations were carried out to investigate the true dispersion state of LDHs in PVC matrix, as shown in Figure 8(b–d). Neither CO<sub>3</sub>-LDH nor Cl-LDH dispersed homogeneously in PVC matrix, the pristine LDH particles could be seen everywhere. In the case of PVC/DS-LDH composites; however, the low aspect ratio LDH galleries are dispersed disorderly and homogeneously in matrix [in Fig. 8(d)]. Additionally, the lateral size of LDH platelets observed is extremely lower than that of pristine LDHs, which may be explained by the fragile nature of the LDH particles.<sup>39</sup>

The thermal stability time of PVC/LDH (CO<sub>3</sub><sup>2-</sup>/Cl<sup>-</sup>/DS<sup>-</sup>) composites measured by Congo Red tests are shown in Figure 9. As the anion exchange reactions were carried out step by step, the thermal stability time of PVC/LDH composites are surprisingly dropped dramatically. This is in contrast to the results by Liu et al.,<sup>5</sup> but in consistence with those



**Figure 9** Thermal stability time of 3 wt % CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, and DS<sup>-</sup>-LDH/PVC composites measured by Congo Red tests.

by Lin et al.<sup>1</sup> It is believed that the HCl adsorption capacity of LDHs plays a key role in dehydrochlorination. Since the interlayer CO<sub>3</sub><sup>2-</sup> is very important in the reaction of HCl, the overall adsorption capacity of HCl falls with the decarbonation and further anion exchange. Therefore, the thermal stability time of PVC/LDH composites decreases.

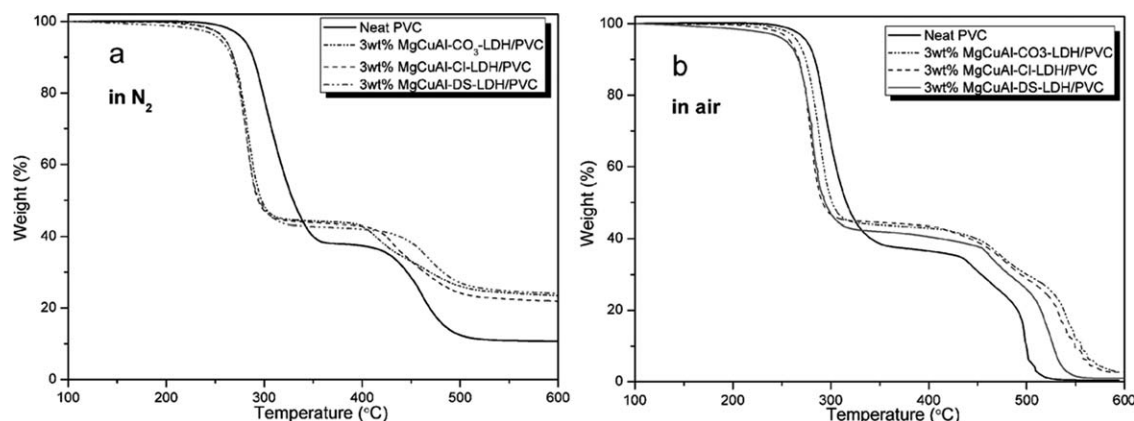
Figure 10 shows TGA curves of PVC/LDH-CO<sub>3</sub><sup>2-</sup>/Cl<sup>-</sup>/DS<sup>-</sup> composites in N<sub>2</sub> (a) and air (b) at heating rate of 10°C/min. In N<sub>2</sub>, TGA curves of PVC/Cl-LDH and PVC/DS-LDH composites do not show significant difference from that of PVC/CO<sub>3</sub>-LDH composite in terms of facilitating dehydrochlorination while increasing char residues significantly. It can be seen that PVC/DS-LDH composite shows different thermal behavior in N<sub>2</sub> and air. In air, PVC/DS-LDH composite is less stable than PVC/CO<sub>3</sub><sup>2-</sup> (or Cl<sup>-</sup>)-LDH composites. Because of the decomposition of interlayer DS long chains at about 400°C, DS<sup>-</sup>-LDH does not show any contribution to

the enhancement of thermal stability of PVC. In N<sub>2</sub>, however, DS could participate in the formation of crosslinked chars thus preventing polymer chains from thermal degradation. In general, to a certain extent, anion exchange and organomodification could not improve the thermal stability of PVC composites although exfoliated LDH/PVC nanocomposites could be achieved.

## CONCLUSIONS

In this study, MgAl-LDH and MgCuAl-LDH with high crystallinity and large platelets have been successfully synthesized by urea hydrolysis method. The addition of carbonated LDHs into PVC matrix significantly increases its thermal stability time while decreases the dehydrochlorination temperature. When compared with MgAl-LDH, carbonated MgCuAl-LDH enhances the thermal stability time of PVC composites by 50% but decreases the 40% weight loss temperature by about 20°C in both N<sub>2</sub> and air. The increased content of polyene sequences and decomposition at higher temperature indicate the potential flame retardant effect of LDH/PVC composites. PVC/MgCuAl-LDH composites show significant smoke suppression effect. The optical density of smoke generated by PVC/MgCuAl-LDH composites is 25% lower than that of PVC/MgAl-LDH.

Through anion exchange, dodecylsulfate intercalated copper-containing LDH with *d*-spacing of 2.54 nm and exfoliated PVC/DS-LDH nanocomposites were prepared. Interestingly, anion-exchanged LDH/PVC composites do not show any advantages in enhancing their thermal stability than those in carbonated form. It is again proved that CO<sub>3</sub><sup>2-</sup> is of importance in enhancing thermal stability of PVC resins.



**Figure 10** TGA curves of neat PVC and 3 wt % CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, and DS<sup>-</sup>-LDH/PVC composites in N<sub>2</sub> (a) and air (b) at heating rate of 10°C/min.



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