Effects of MgAlCe-CO₃ Layered Double Hydroxides on the Thermal Stability of PVC Resin

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ABSTRACT: MgAlCe-CO₃ layered double hydroxides (LDHs) with different Ce/Al molar ratios were prepared by the constant pH coprecipitation method. The synthesized materials were characterized by XRD and FTIR, and the results showed that the hydrotalcite-like materials have a layered structure. Different LDHs as stabilizers were mixed with PVC resin. The tests of thermal aging and Congo red for the PVC composites were carried out at 180 ± 1°C, respectively. The results showed when MgAlCe-CO₃-LDHs were added into PVC as single thermal stabilizers, 3 phr (parts per hundred PVC resin) MgAlCe-CO₃-LDH with Ce/Al (molar ratio) = 0.075 has a better stabilizing effect on PVC than others. Compared

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.^{1,2} However, one major drawback of PVC is that it decomposes at a temperature lower than its processing temperature. Thermal degradation of PVC involves a complex chain dehydrochlorination reaction, which may produce an undesirable color in the material.^{3,4} 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.⁵ Therefore, metal soaps, rare earth stabilizers, hydrotalcitelike materials, and other nontoxic thermal stabilizers have played important roles in this field.

with single thermal stabilizers (LDHs or Ca/Zn systems), the composite thermal stabilizers including 0.3 g calcium stearate (Cast₂), 1 g zinc stearate (Znst₂), and 3 g MgAlCe-CO₃-LDH have significantly enhanced the thermal stability of PVC sample, and the thermal stable time was over 190 min. The main reason could be concluded to the special structure of Ce element and the synergistic reaction among MgAlCe-CO₃-LDHs, Cast₂, and Znst₂. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2620–2626, 2011

Key words: MgAlCe-CO3-LDHs; poly(vinyl chloride); thermal stabilizers; degradation

Metal soaps, also known as fatty acid salts, have an unconspicuous effect on thermal stability of PVC resin. However, their transparency and the lubricity are excellent.⁶ The thermal stability is not favorable when metal soaps are employed alone, so it is generally used as an assistant thermal stabilizer in combination with other thermal stabilizers.^{7,8}

Rare earth thermal stabilizer is a new-type stabilizer with many advantages, such as high efficiency, nontoxic, and it has a good synergetic effect with other stabilizers.⁹ The rare earth thermal stabilizers present favorable stabilization, because the rare earth ion ($RE^{\delta+}$) can react with the labile chlorine atoms (CI^{r-}) to form a stable coordinate complex and scavenge HCl effectively.¹⁰ However, the rare earth stabilizers usually exhibit poor initial stabilization effects. In combination with other stabilizers and assistant reagents, the stabilization effect of rare earth stabilizers can be improved remarkably.^{11,12}

Layered double hydroxides (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. 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 application prospect.^{13–15} In recent years, LDHs

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have attracted much attention for efficient additives to enhance PVC thermal stability.^{16,17}

Based on the special structures and thermal stabilizing mechanisms of rare earth elements and hydrotalcite-like materials, MgAlCe-CO₃-LDHs were prepared by the constant pH coprecipitation method in this study. MgAlCe-CO₃-LDHs together with metal soaps (both Cast₂ and Znst₂) were mixed with PVC, and then the thermal stability of PVC composites was studied by static thermal aging test and Congo red test. The thermal effects of the composite thermal stabilizers were compared with other single thermal stabilizers, and the synergistic effect and the thermal stabilizing mechanisms of thermal stabilizers were also discussed.

EXPERIMENTAL

Materials

The PVC resin (SG-5 type, suspension grade) was kindly provided by Beijing Huaer Company Limited. All of the chemical reagents used in this study are of A.R. grade. The deionized water was distilled twice to get rid of carbon dioxide (CO_2).

Preparation of MgAl-CO₃-LDHs

Mixed salt solutions containing Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (with Mg²⁺/Al³⁺ molar ratios of 2.0), and a mixed solution containing NaOH and Na₂CO₃ were synchronously added slowly to the deionized water at a speed of 1 drop/s, respectively, under vigorous stirring at 85°C. The mixture was stirred for 4 h under a constant PH value. Subsequently, the white resultant suspension was aged. The precipitate was then filtered and washed with deionized water. Finally, the precipitate was grinded to fine powder after drying.

Preparation of MgAlCe-CO₃-LDHs

At first, the Mg(NO₃)₂·6H₂O solution was added into the solution containing Al(NO₃)₃·9H₂O and Ce(NO₃)₃·6H₂O to form a aqueous mixture. The total concentration of Al(NO₃)₃·9H₂O and Ce(NO₃)₃·6H₂O in the aqueous mixture was fixed at the value of 1 mol/L. Then, the aqueous mixture above and a mixed solution containing NaOH and Na₂CO₃ were added into deionized water at a speed of 1 drop/s, respectively. The solution was stirred for 4 h at 85°C under a constant pH value. Subsequently, the resulting slurry was aged, filtered, washed and dried.

Characterization techniques for MgAlCe-CO₃-LDHs

X-ray diffraction (XRD) patterns were recorded on Rigaku D/max-2500 diffractometer (40 kV, 100 mA) using Cu K α radiation at a scanning rate of $2\Theta = 8^{\circ}/$ min. FTIR spectra were performed on a Nicolet Nexus-670 FTIR spectrometer (as KBr discs, with wavenumber 400–4000 cm⁻¹, resolution 0.09 cm⁻¹, and the weight of measured sample 2 mg.). The surface morphology of synthesized MgAlCe-CO₃-LDHs was observed using scanning electron microscope (JSM-6360LV).

Procedure for thermal stability

Static thermal aging test

Mixtures containing PVC powder, dioctylphthalate (DOP), different LDHs, Cast₂, and Znst₂ were blended in a double-roller mixer for 5 min at 180°C. The resulting composites were molded to sheets with a thickness of 1.0 mm and cut into 3 cm \times 2 cm strips. These strips were placed in a Thermal Aging Test Box at 180 \pm 1°C and subjected to static thermal aging. The strips were taken out of the box every 10 min and subjected to visual examination. The time that black decomposition started to emerge was defined as the thermal stability time of PVC.

Congo red test

PVC and other different stabilizers were mixed absolutely in the mortar. The resultant mixtures were put into a tube with Congo red test paper located at 2 cm above the sample. The tube was immersed into an oil bath at $180 \pm 1^{\circ}$ C for evaluating static thermal stability of PVC composites. The time required for the color change from red to blue was taken to be the stability time. Each sample was measured three times and the average time was obtained.

RESULTS AND DISCUSSION

Characterization of the MgAlCe-CO₃-LDH series

FTIR analysis of MgAl-CO₃-LDH and MgAlCe-CO₃-LDH

For the samples of MgAlCe-CO₃-LDH [Fig. 1(a)] and MgAl-CO₃-LDH [Fig. 1(b)] the FTIR spectra shown in Figure 1 are very similar. The introduction of rare earth element to MgAlCe-CO₃-LDH results in slight peak shift. The broad peak around 3459 cm⁻¹ in Figure 1(a) can be ascribed to the stretching of OH groups attached to metal ions. The bending vibration of interlayer water is found at 1650 cm⁻¹. The antisymmetric vibration of CO32- appears at 1365 cm-1. The lower wavenumber bands at 400–700 cm^{-1} is due to LDH lattice vibrations (Mg-O, Al-O, Ce-O, Ce-O-Mg). The bands at 776 and 555 cm^{-1} can be assigned to Al-O stretching modes. These Al-O peaks of MgAlCe-CO₃-LDH are weaker than those of MgAl-CO₃-LDH, which probably resulted from the partial replacement of Ce^{3+} .



Figure 1 FTIR spectras of MgAl-CO₃-LDH and MgAlCe-CO₃-LDH. (the transmittance of some weakening peaks are mentioned in the round brackets). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XRD analysis of MgAl-CO₃-LDH and MgAlCe-CO₃-LDH

The XRD patterns of MgAl-CO₃-LDH and MgAlCe-CO₃-LDH are shown in Figure 2. The XRD patterns of MgAlCe-CO₃-LDH and MgAl-CO₃-LDH show almost identical characteristics. The characteristic reflections (003), (006), (009), and (110) are easily recognized in both patterns. It can be seen in Figure 2 the diffraction peaks are sharp and symmetrical, the baseline is low and stable, indicating the relatively well-formed crystalline layered structures. Compared with MgAl-CO₃-LDH, there is a weak peak at 2 Θ value of about 28.5°, which corresponds to the characteristic peak of Ce(OH)₃.¹⁸ (JCPDS card no.74-0665).

SEM micrograph of MgAlCe-CO₃-LDH

Typical SEM micrograph of MgAlCe-CO₃-LDH is shown in Figure 3. This figure indicates the existence of lamellar particles looks like rounded hexagonal shape, which is typical of hydrotalcite-like materials.

Thermal stability testing of prepared PVC composites

Effect of varying the Ce/Al molar ratio for MgAlCe-CO₃- LDHs on the PVC stability

The effect of mixtures containing 100 g PVC, 50 g DOP, and 3 g MgAlCe-CO₃-LDHs with different Ce/Al molar ratios on the thermal stability of PVC are illustrated in Figure 4 by static thermal aging test.

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Figure 2 XRD patterms of MgAl-CO₃-LDH and MgAlCe-CO₃-LDH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 4(a), pure PVC without any stabilizer begin to color even during the mixing process and become black after only 20 min at 180 \pm l°C.

Chlorine containing polymers like PVC undergo an autocatalytic dehydrochlorination reaction under the influence of temperatures and energy rich radiation. It is suggested that an initial reaction of dehydrochlorination at a lower temperature probably autoaccelerates the evolution of HCl via two mechanisms:^{19,20} (1) at the beginning, the formation of a double bond activates the subsequent loss of HCl from an adjacent unit to form a conjugated bond system; (2) the primary HCl molecule takes part in the formation of a dehydrochlorination transition state, which results in an autocatalytic dehydrochlorination. The degradation temperature and yield



Figure 3 SEM micrograph of MgAlCe-CO₃-LDH.



Figure 4 Effects of MgAlCe-CO₃-LDHs with Ce/Al molar ratios of (a) PVC, (b) 0, (c) 0.025, (d) 0.05, (e) 0.075, and (f) 0.1 on the thermal stability of PVC composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature for PVC are very close so that many problems occur during PVC processing. Therefore it is necessary to add thermal stabilizers to PVC resin to improve their thermal stability.²¹

The thermal stability results for the PVC samples containing MgAl-CO₃-LDH (Ce/Al=0) are shown in Figure 4(b). The stability time is longer than pure PVC although the initial coloring is still serious.

The reaction between MgAl-CO₃-LDH and HCl occurs in a two-step process.²² First of all, the counterions between the LDH layers are apt to react with the HCl gas. And then, the LDH itself reacts with HCl under complete destruction of the LDH structure and formation of metal chlorides. The MgAl-CO₃-LDH can not react with labile chlorine atoms (such as allyl chloride), so it is difficult to restrain the initial coloring and prevent the growth of "Polyolefin Structure" when it is used alone. As the electronegativity from Mg to Ba is low and close to each other, the capacity of electronic absorption of Mg is very weak. So the labile chlorine atoms with which Mg can not form coordinate bond will not be replaced, and the degradation of PVC is easy to carry out.²³ The MgAl-CO₃-LDH can absorb HCl well only when there is a considerable number of

HCl in the PVC system. Therefore, the initial coloring is very serious when the MgAl-CO₃-LDH was used as thermal stabilizer individually.

The thermal stabilities of mixtures containing PVC resin, DOP, and MgAlCe-CO₃-LDHs with different Ce/Al molar ratios are shown in Figure 4(c–f), respectively. Compared with Figure 4(b). the long-term thermal stability is enhanced although the initial coloring is restrained just a little. The thermal stability of the PVC samples becomes better with increasing Ce/Al molar ratio. When the ratios of Ce/Al became higher than 0.075, however, there was a slight decrease in thermal stability. So it is suggested that 0.075 (n(Ce)/n(Al)) is the optimum ratio.

Compared with the PVC strips containing MgAl-CO₃-LDH, the long-term stabilization effect of PVC composites containing MgAlCe-CO3-LDHs are more excellent although the early coloring maintains just a little better. The effect about thermal stabilization of rare earth on PVC is attributed to the strong complexation property of rare earth elements, which have longer atom radius and more coordination numbers.²⁴ According to the conception of Lewis' acid and alkali, rare earth ions belong to hard-acid, and they are inclined to coordinate with the hard-alkali chloride ions in PVC main chains.²⁵ Consequently, MgAlCe-CO3-LDHs are very effective in coordinating with allylic chlorine atoms and inhibiting degradation of PVC resin. At the same time, they can scavenge HCl as the MgAl-CO₃-LDH does. As the higher activation energy of complexing Cl⁻ for rare earth complex, it still showed the initial coloring. So it is necessary to combine the MgAlCe-CO₃-LDHs with other thermal stabilizers, which are good at short-term stabilization in order to get a good synergetic effect.

Effect of varying the amount of MgAlCe-CO₃-LDHs on the stability of PVC

PVC (100 g), DOP (50 g), and varying amounts (in the range of 2–5 g) of MgAlCe-CO₃-LDHs (n(Ce)/n(Al) = 0.075) were mixed. The results of static thermal aging tests at 180 ± l°C are shown in Figure 5. There is a remarkable improvement in thermal stability with increasing of the MgAlCe-CO₃-LDHs amount from 2 to 3 phr (parts per hundred resins). However, further increment of MgAlCe-CO₃-LDHs in PVC can not enhance the thermal stability any more, but weaken it instead, suggesting that the optimum amount of MgAlCe-CO₃-LDHs fillers is 3 phr.

Effect of composite thermal stabilizers on the stability of PVC

 $Cast_2/1$ g Znst_2 (0.3 g) and DOP (50 g) were added into 100 g PVC powder and the thermal aging test



Figure 5 Effects of MgAlCe-CO₃-LDHs at (a) 2 phr, (b) 3 phr, (c) 4 phr, (d) 5 phr on the thermal stability of PVC composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results are shown in Figure 6(a). There is a very good initial coloring, however, the composites turn black suddenly. It is showed that the blackening was observed after 90 min.

Ca/Zn stabilizers have synergistic effect and present favorable stabilization.^{26,27} Zinc stearate has strong Lewis acidity, which can scavenge HCl and react with labile chlorine atoms. The unsuitable production of the reaction is the ZnCl₂, which can result in a sudden dehydrochlorination of PVC.²⁸ However, it has been claimed that the reaction between ZnCl₂ and Cast₂ occurs only after ZnCl₂ concentrations reach a certain level. Conversely, CaCl₂ production does not promote sudden dehydrochlorination.²⁹ So the initial coloring is good. However, with the increase of ZnCl₂, it is suggested that the sample

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turns black suddenly and has some disadvantages in long-term stability due to the marked "zinc burning".^{30,31}

Considering favorable short-term and long-term stabilization effects of the Cast₂/Znst₂ system and the MgAlCe-CO₃-LDHs stabilizers, a combination of these two kinds of stabilizers might play a significant role in enhancing the short-term and long-term stability of PVC. The thermal stabilities of composites



Figure 6 Thermal stability of composites of (a) PVC + $Cast_2 + Znst_2$, (b) PVC + $Cast_2 + Znst_2 + MgAl-CO_3-LDH$, (c) PVC + $Cast_2 + Znst_2 + MgAlCe-CO_3-LDH$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 7 Schematic diagrams of the formation of d-d orbitals.

containing 100 g PVC powder, 0.3 g Cast₂/1 g Znst₂, 50 g DOP, and 3 g MgAlCe-CO₃-LDH, are shown in Figure 6(c). The thermal stability is significantly improved compared to samples of Figure 6(b) containing 3 g MgAl-CO₃-LDH, 0.3 g Cast₂/1 g Znst₂, and 50 g DOP, and the coloring is restrained for over 190 min. It is obvious that the initial coloring is also better than other thermal stabilizers.

The Cast₂/Znst₂ system and the MgAlCe-CO₃-LDH stabilizer have synergistic effect and present favorable stabilization. The orbit theory might be introduced to explain the results.³² The outermost d orbitals of Ce³⁺ and Ca²⁺ are "unoccupied orbitals", on which there are no electrons. Conversely, the 3d orbitals of Zn²⁺ are full of electrons, which are called "occupied orbitals". It is clear that the thermal stability is excellent when the "unoccupied orbitals" combined with the "occupied orbitals". According to the Hund's Rule, every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin. In this state, the atomic structure is relatively stable. Immediately, the

TABLE I
The Effect of MgAlCe-CO ₃ -LDHs with Different Ce/Al
Molar Rations on the Thermal Stability of PVC at 180 ±
1°C (as Determined by Congo Red Test)

PVC composite	nCe/nAl	Thermal stable time of PVC composite (min)
PVC	_	15
PVC+MgAl-CO ₃ -LDHs	0	56
PVC+MgAlCe-CO ₃ -LDHs	0.025	75
PVC+MgAlCe-CO ₃ -LDHs	0.05	97
PVC+MgAlCe-CO ₃ -LDHs	0.075	158
PVC+MgAlCe-CO ₃ -LDHs	0.1	92

relatively stable complex consisting of several d-d shared electron pairs was formed, which is probably due to the fact that the outermost d orbitals of Ce³⁺ and Ca^{2+} are combined with the 3d orbitals of Zn^{2+} respectively. When the complexes are formed, the d orbitals were all under the condition of "half-occupied". Consequently, the lively zinc chloride was changed into a more stable d-d complex. The formation of d-d orbitals is shown in Figure 7. In addition, the Ce element has many unoccupied orbitals, which can accept lone pair electrons of ligands, so the Ce element is very effective in coordinating with the labile chloride ions in PVC main chains and inhibiting degradation of PVC resin. At the same time, the special layered structure is inclined to scavenge HCl as the MgAl-CO₃-LDH does. Based on the common effect of Cast₂, Znst₂, and MgAlCe-CO₃-LDHs, the PVC composites present favorable stabilization.

The results of congo red test

The ability of thermal stabilizers to absorb HCl is reflected in the Congo red test. The results are shown in Tables I–III. As shown in these tables, the

TABLE II
The Effect of MgAlCe-CO ₃ -LDHs with Different
Amount on the Thermal Stability of PVC at 180 ± 1°C
(as Determined by Congo Red Test)

	The amount of MgAlCe-CO ₃ -LDHs	Thermal stable time of PVC
PVC composite	(phr)	composite (min)
PVC+MgAlCe-CO ₃ -LDH	s 2	136
PVC+MgAlCe-CO ₃ -LDHs	s 3	158
PVC+MgAlCe-CO3-LDHs	5 4	115
PVC+MgAlCe-CO ₃ -LDHs	s 5	114

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TABLE IIIThe Effect of Composite Thermal Stabilitizers on theThermal Stability of PVC at 180 ± 1°C (as Determinedby Congo Red Test)

PVC composite	Thermal stable time of PVC composite (min)
PVC+Cast ₂ +Znst ₂	81
PVC+MgAl-CO ₃ -LDH+Cast ₂ +Znst ₂	101
PVC+MgAlCe-CO ₃ -LDH+Cast ₂ +Znst ₂	202

stability time of PVC samples containing single MgAl-CO₃-LDH is longer than pure PVC, but shorter than PVC composite containing single MgAlCe-CO₃-LDH. Compared with single stabilizers, the PVC composites containing Cast₂, Znst₂, and MgAlCe-CO₃-LDH can lead to a more significant enhancement in improving the thermal stability. These results of Congo red test are in good agreement with those of the static thermal aging tests. The time when Congo red test paper began to turn blue and the strips of the static thermal aging tests turn black is approximately equal.

CONCLUSIONS

- 1. The MgAlCe-CO₃-LDHs were prepared by the constant pH coprecipitation method, and the results showed that the hydrotalcite have a layered structure.
- 2. The PVC composites containing MgAlCe-CO₃-LDHs only show a better thermal stability, when the amount of MgAlCe-CO₃-LDH filler is 3 phr and the molar ratio of Ce/Al is 0.075.
- 3. The PVC composites containing 100 g PVC, 50 g DOP, 0.3 g Cast₂/1 g Znst₂, and 3 g MgAlCe-CO₃-LDH lead to a significant enhancement in improving the thermal stability. The results reveal that the blackening is restrained for more than 190 min, which can be sumed up to the special structure of Ce element and the "synergistic reaction" among MgAlCe-CO₃-LDHs, Cast₂ and Znst₂.

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