

Lanthanum histidine with pentaerythritol and zinc stearate as thermal stabilizers for poly(vinyl chloride)

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ABSTRACT: Lanthanum histidine [$\text{La}(\text{His})_2 \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or $\text{La}(\text{His})_2$] was synthesized via the reaction of histidine and lanthanum nitrate, and it was investigated as a stabilizer for poly(vinyl chloride) (PVC). The results show that $\text{La}(\text{His})_2$ exhibited a stabilizing effect on PVC as a long-term stabilizer because it prolonged the stability time of PVC to 76 min, which was about 24 times longer than the stability time of the pure PVC. The stabilizing effect of $\text{La}(\text{His})_2$ as a costabilizer with pentaerythritol (Pe) and zinc stearate (ZnSt_2) was also studied. The results show that the use of $\text{La}(\text{His})_2$ with Pe or Pe/ ZnSt_2 improved the stability time of PVC. $\text{La}(\text{His})_2/\text{Pe}/\text{ZnSt}_2$ provided PVC with a good initial color and long-term stability, and when it was prepared at mass ratios of 0.8:2.4:0.8 and 1.6:1.6:0.8, the stability times of PVC were improved to 86 and 88 min, respectively. As a nontoxic stabilizer, $\text{La}(\text{His})_2/\text{Pe}/\text{ZnSt}_2$ has the potential to replace the toxic stabilizers widely used in PVC manufacturing. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42878.

KEYWORDS: degradation; poly(vinyl chloride); thermal properties

Received 19 January 2015; accepted 20 August 2015

DOI: 10.1002/app.42878

INTRODUCTION

Poly(vinyl chloride) (PVC) is a low-cost, versatile, and commercially available thermoplastic polymer. It has wide applications in daily life. However, because of the structural defects in the polymeric chains of PVC (e.g., branching, chloroallyl groups, end groups, head-to-head structures^{1–3}), the thermal stability of PVC is poor. During thermal processing, PVC always undergoes autocatalytic dehydrochlorination, and conjugated double bonds form on the polymer chains.⁴ The presence of conjugated double bonds leads to discoloration and poor mechanical properties in PVC. Thus, thermal stabilizers, such as lead salt, Ca/Zn salts, and organotin compounds have been used to keep PVC from thermally degrading.^{5–7} Stabilizers can act in two ways: (1) they can react with the hydrogen chloride (HCl) emitted by degraded PVC, and (2) they can replace the unstable chlorine on the PVC backbone with other stable groups.^{8–10}

The use of highly effective lead-based or organotin compound stabilizers has been restricted to protect the environment from pollution. Thus, research into nontoxic stabilizers for PVC is of great interest. Organic compounds with specific functional

groups, such as vanillin Schiff's bases, uracil derivatives, and soy protein, have been studied as PVC stabilizers.^{11–13} Metallic complexes, such as zinc compounds and rare earth compounds, have also showed potential to be applied as PVC stabilizers.^{14–16} Rare earth compounds are regarded as highly effective multiple-use stabilizers that can improve the long-term stability and processing properties of PVC, and they are nontoxic.^{17–19} However, rare earth stabilizers cannot provide PVC with good initial color in the thermal process, and they are used with other stabilizers to overcome this shortcoming.

In this study, lanthanum histidine [$\text{La}(\text{His})_2 \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ or $\text{La}(\text{His})_2$] was evaluated as a PVC stabilizer. Histidine is one of the essential amino acids present in humans and other mammals. It has an imidazole and an amino functional group; these have the ability to react with HCl, and thus, we expected the compound of histidine and the rare earth element $\text{La}(\text{His})_2$ to improve the stability time of PVC. The use of $\text{La}(\text{His})_2$ with other commercial stabilizers of PVC is also interesting. The thermal stabilizing effects of $\text{La}(\text{His})_2$ on PVC were investigated, and the costabilizing effects between $\text{La}(\text{His})_2$ and pentaerythritol (Pe) and zinc stearate (ZnSt_2) were also studied.

Additional Supporting Information may be found in the online version of this article.

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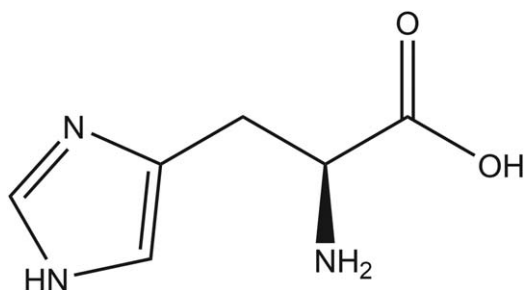


Figure 1. Structure of histidine.

EXPERIMENTAL

Materials

PVC (SG-5) was from Sea Level Polymer Industry Co., Ltd. (Baotou, China). Histidine was from Vetec (Wuxi, China; Figure 1). Sodium hydroxide (NaOH) and lead stearate (PbSt₂) were from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). Commercially pure calcium stearate and ZnSt₂ were from Tianjin 3rd Chemical Reagent Factory (Tianjin, China). Pe was from Puyang Wangda Chemical Co., Ltd. (Puyang, China). Lanthanum oxide (La₂O₃) was from Baotou Rare Earth High Technology Co. (Baotou, China). Nitric acid was from the Kemiou Chemical Reagent Co. (Tianjin, China). Lanthanum nitrate and lanthanum stearate (LaSt₃) were synthesized in our laboratory as follows.

An amount of La₂O₃ (ca. 30 g) and 50 mL of deionized water were added to a 250-mL beaker, and diluted nitric acid was added dropwise at 60°C. The mixture was stirred until La₂O₃ dissolved completely. The pH of the solution was adjusted to 2.0–3.0, and a lanthanum nitrate solution was obtained. The concentration of the solution was determined by ethylenediamine tetraacetic acid titration.

LaSt₃ was prepared with a double decomposition method.¹⁶ Stearic acid (4.5 g) was added to 100 mL of distilled water, and the mixture was heated to 80°C under stirring. Then, 0.6 g of NaOH was dissolved in the stearic acid solution, and stearic acid salt was generated. The mixture was stirred at 80°C for about 20 min, and 3.7 mL of an La(NO₃)₃ solution (1.35M) was added dropwise into the solution. The reaction proceeded for 30 min, and the obtained mixture was filtered, washed with distilled water, and dried at 70°C for 8 h.

Synthesis of La(His)₂

Histidine (1.55 g) and NaOH (0.4 g) were dissolved in 20 mL of deionized water, and 3.7 mL of lanthanum nitrate solution (1.35M) was added. The solution was stirred vigorously for 20 min and kept in a water bath at 90°C until the volume of the solution decreased to 10 mL via evaporation. A white precipitate was present when the solution was cooled down to room temperature; this was coarse La(His)₂. The coarse product was dissolved in water again, and the solution was concentrated to about 15 mL. Ethanol (ca. 10 mL) was added to the solution to precipitate La(His)₂. The precipitate was collected by filtration and washed with ethanol. After 8 h of drying at 70°C, the refined La(His)₂ was obtained.

The lanthanum content of La(His)₂ was measured by ethylenediamine tetraacetic acid titration with xylenol orange as the indicator, and the contents of carbon, hydrogen, and nitrogen were determined with a Vario EL III Elementar instrument (the content of oxygen was determined by subtraction). Fourier transform infrared (FTIR) spectra of the samples were obtained on an IR spectrophotometer (Bruker Alpha) in the range 4000–400 cm⁻¹ with a KBr disc.

Congo Red Test

To evaluate the static thermal stability of PVC with different stabilizers, 2.5 g of PVC and 0.1 g of stabilizer were mixed in a mortar. The resulting mixture was put into a tube with Congo red test paper located 2 cm above the sample. The tube was heated in an oil bath at 180°C. The time taken for the Congo red test paper to begin to turn blue was defined as the stability time.¹⁹

Discoloration Test

The efficiencies of the stabilizers were evaluated by a comparison of the color changes of PVC samples containing different stabilizers after heating at 180°C for different times. Briefly, 2.5 g of PVC and 0.1 g of stabilizer were mixed in a mortar. The resulting mixture was separated into six to eight porcelain plates and put into an oven at 180°C. After 15 min, one plate was examined every 10 min until all of the samples were measured.

Thermogravimetric Analysis (TGA)

Plain PVC powder and PVC samples that contained stabilizer (4% mass ratio) were measured on a thermogravimetric analyzer (STA229C, Netzsch, Germany). The temperature was increased from room temperature to 700°C at a heating rate of 10°C/min in an argon atmosphere.²⁰

RESULTS AND DISCUSSION

Characterization of La(His)₂

The complex was characterized by elemental analysis, and the metal ion was determined by a titrimetric method. The contents of carbon, hydrogen, nitrogen, lanthanum, and oxygen of the synthesized La(His)₂ were 26.43, 3.82, 17.57, 25.86, and 26.32%, respectively. Thus, the molecular formula was likely to be La(His)₂·(NO₃)₂·2H₂O because the theoretical contents of carbon, hydrogen, nitrogen, lanthanum, and oxygen were 26.42, 3.66, 17.98, 25.50, and 26.42%, respectively. The values were consistent with experimental data shown previously.

FTIR spectra of La(His)₂ and histidine are shown in Figure 2, and the peak assignments are shown in Table I. Compared with the spectrum of histidine, the peaks representing asymmetric and symmetric stretching vibrations of COO⁻ in the spectrum of La(His)₂ shifted from 1590 and 1410 cm⁻¹ to 1570 and 1417 cm⁻¹.^{21,22} This change was attributed to the generation of lanthanum salts. The peaks at 1320 and 996 cm⁻¹ in the spectrum of La(His)₂ represented the wagging vibrations of CH₂ and deformation vibrations of the ring structure. The asymmetric deformation vibrations of NH₃⁺ (1632 cm⁻¹) were not present in the spectrum of La(His)₂ because the NH₃⁺ group reacted with NaOH to form NH₂, and the peak of NH₂ was overlapped

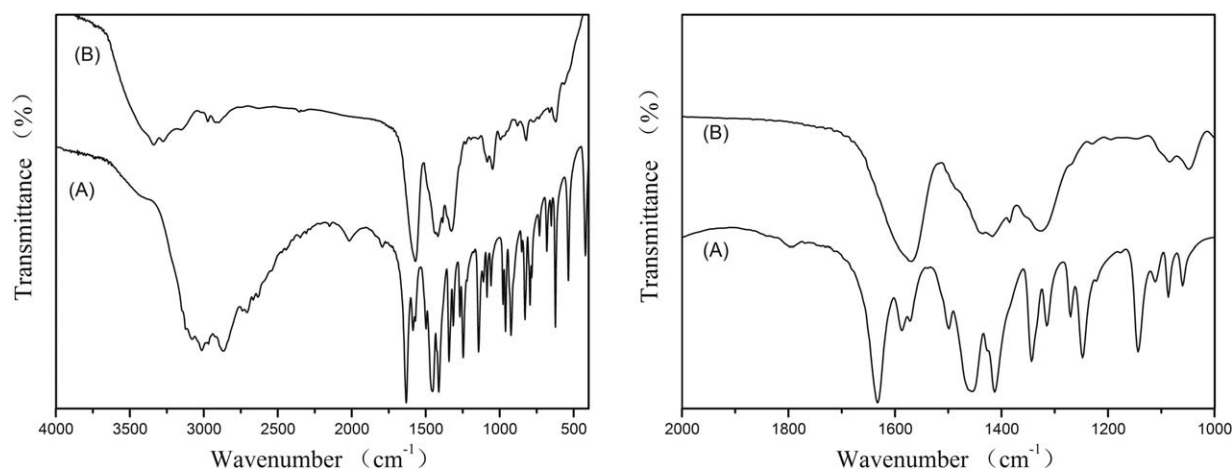


Figure 2. FTIR spectra of (A) histidine and (B) $\text{La}(\text{His})_2$ in the ranges 4000–400 cm^{-1} (left) and 2000–1000 cm^{-1} (right).

by the band at 1570 cm^{-1} . These results show that $\text{La}(\text{His})_2$ was synthesized successfully.

Effects of $\text{La}(\text{His})_2$ and Histidine as Thermal Stabilizers of PVC

The stability times of the PVC samples containing $\text{La}(\text{His})_2$ as stabilizers are shown in Table II. The stability times of PVC without any stabilizer and PVC samples stabilized by histidine, LaSt_3 , and Ca/ZnSt_2 (mass ratio = 3:1) are shown for comparison. The results illustrate that histidine alone prolonged the stability time of PVC, and this efficiency was comparable with those of LaSt_3 and Ca/ZnSt_2 . $\text{La}(\text{His})_2$ showed a good stabilizing effect in this test, and it improved the stability time of PVC to more than two times longer than that of PVC containing histidine or LaSt_3 .

The results of the discoloration test are summarized in Table III. The samples containing $\text{La}(\text{His})_2$ were discolored in the early stage, and the color was darker than that of pure PVC. This result was unusual because PVC containing other stabilizers showed a lighter color than the pure PVC after a thermal process. However, there was only a slight color change in the samples containing $\text{La}(\text{His})_2$ in the 35–65-min duration; this

indicated a potential long-term stabilizing effect of $\text{La}(\text{His})_2$. The samples containing histidine performed poorly in this test.

The TGA curves of the pure PVC and PVC stabilized with 4% stabilizers may explain the previous results (Figure 3). The weight loss within the temperature range 200–350°C was mainly related to dehydrochlorination in the PVC backbone;²³ this was important for evaluating the thermal stability of PVC. PVC with histidine or $\text{La}(\text{His})_2$ stabilizers began losing weight at temperatures lower than that of pure PVC; this illustrated that histidine and $\text{La}(\text{His})_2$ catalyzed the degradation of PVC in the early stages of a thermal process. This catalyzing effect caused PVC with histidine or $\text{La}(\text{His})_2$ to discolor easily in the early stages during the discoloration test.

We also found that pure PVC retained 41.6% of its original weight at 335°C; at the same temperature, PVC stabilized by $\text{La}(\text{His})_2$ retained more weight (43.4%) than pure PVC. The greater residual weight was attributed to $\text{La}(\text{His})_2$ absorbing HCl emitted by the degrading PVC. [The explanation of this part, which included the proposed reaction of $\text{La}(\text{His})_2$ with HCl, the discussions, the assumptions, and the calculating equation,

Table I. Peak Assignments for FTIR Spectra of Histidine and $\text{La}(\text{His})_2$

Peak position: Histidine	Peak position: $\text{La}(\text{His})_2$	Assignment
1632 cm^{-1}		NH_3^+ asymmetric deformation vibrations
1590 cm^{-1}		COO^- asymmetric stretching vibrations
	1570 cm^{-1}	COO^- asymmetric stretching vibrations
1500 cm^{-1}		NH_3^+ symmetric stretching vibrations
1457 cm^{-1}		CH_2 deformation
	1417 cm^{-1}	COO^- symmetric stretching vibrations
1410 cm^{-1}		COO^- symmetric stretching vibrations
1346 cm^{-1}		CH_2 wagging vibrations
	1320 cm^{-1}	CH_2 twisting vibrations
1315 cm^{-1}		CH_2 twisting vibrations
992 cm^{-1}		Deformation vibrations of the ring structure
	996 cm^{-1}	Deformation vibrations of the ring structure

Table II. Stability Times of PVC with Different Stabilizers at 180°C

Stabilizer	Stability time (min)
Pure PVC	3
LaSt ₃	28
Ca/ZnSt ₂ (3:1)	21
La(His) ₂	76
Histidine	30

is given in the Supporting Information]. Because La(His)₂ absorbed this HCl, the PVC was protected from any rapid degradation caused by HCl, and the concentration of HCl in the system decreased. Thus, the two effects of La(His)₂ mentioned previously contributed to keeping the test paper red for a long time during the Congo red test.

Mechanism of La(His)₂ Stabilization of PVC

We propose that La(His)₂ stabilized PVC by the absorption of the HCl gas released by degraded PVC. To confirm this stabilizing mechanism, we used an Ag(NO₃)₃ test.¹⁵ La(His)₂ was subjected to a stream of HCl gas at 180°C for 40 min. The treated La(His)₂ was heated at 120°C in air for 2 h to remove residual HCl. The resulting product was dissolved in deionized water, and one droplet of 0.1 mol/L Ag(NO₃)₃ solution was added. A white precipitate was formed immediately because there were Cl⁻ ions present in the treated stabilizer; this indicated that La(His)₂ acted as an HCl absorber.

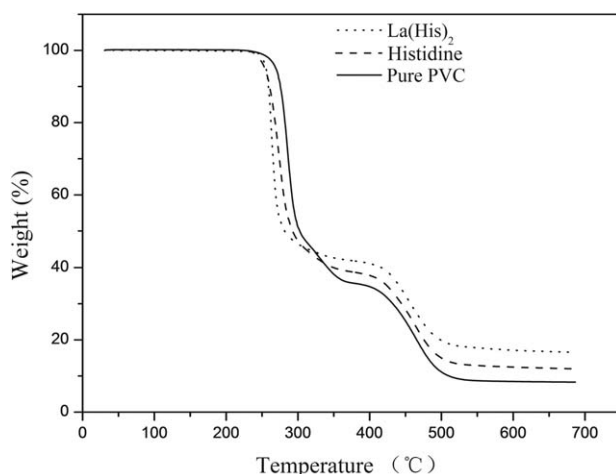
To further study the stabilizing mechanism, La(His)₂ treated by HCl was characterized by FTIR spectroscopy. Histidine, as the ligand of La(His)₂, was also treated with HCl by the same method mentioned previously, and the HCl-treated product was heated at 100°C in air for 2 h to remove residual HCl. The resulting product was also characterized by FTIR spectroscopy for comparison.

Figure 4 shows the IR spectra of histidine and histidine treated by HCl at 180°C. Compared with the spectrum of histidine before treatment, there was a new peak at 1740 cm⁻¹ in the spectrum of histidine treated by HCl. This peak was attributed to C=O stretching vibrations of amino acid hydrochloride.²⁴

Table III. Discoloration of PVC as a Function of the Degradation Time with Heating at 180°C in Air [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stabilizer	Degradation time (min)						
	0	15	25	35	45	55	65
La(His) ₂							
Histidine							
Pure PVC							

PVC, 2.5 g; stabilizer, 0.1 g.

**Figure 3.** TGA curves of the pure PVC and PVC stabilized by histidine and La(His)₂.

This result indicates that histidine reacted with HCl, and histidine hydrochloride was produced.

In the FTIR spectrum of La(His)₂ treated by HCl (Figure 5), the bands at 1620, 1490, and 1142 cm⁻¹ were attributed to the asymmetric deformation vibrations, symmetric deformation vibrations, and rocking vibrations of NH₃⁺, respectively.^{21,24} The band representing asymmetric vibrations of COO⁻ was overlapped by the band at 1620 cm⁻¹, and the band representing asymmetric vibrations of COO⁻ was at 1428 cm⁻¹. There was a weak band at 1740 cm⁻¹ in the spectrum of La(His)₂ treated by HCl; this was similar to that in the spectrum of histidine treated by HCl. All of the previous findings indicate that histidine hydrochloride was generated during the treatment process. From this analysis, the mechanism of La(His)₂ stabilizing PVC is proposed as follows. Lanthanum chloride and histidine were generated after La(His)₂ absorbed HCl, and the generated histidine could also absorb HCl. However, in the early stage of the thermal process, the amino salt (histidine hydrochloride) generated during the stabilizing process may have contributed to the degradation of PVC.²⁵ Therefore, although La(His)₂ provided PVC with long-term stability, the side effect was PVC discoloration in the early stage.

Effects of the Costabilizers on PVC Degradation

The poor performance of La(His)₂ in preventing PVC discoloration indicated that La(His)₂ cannot be used as a PVC stabilizer. However, La(His)₂ could be used as a costabilizer because of its good long-term stabilizing effect. There may be a synergistic effect between La(His)₂ and another stabilizer that also has a good stabilizing effect. We chose ZnSt₂ and Pe as potential costabilizers with La(His)₂, and the effects of the complex stabilizers were investigated.

Effects of La(His)₂/Pe on Stabilizing PVC

The results of the Congo red test and discoloration test on the PVC samples containing La(His)₂/Pe with different mass ratios are shown in Tables IV and V, respectively. From the results of the discoloration test, the samples stabilized by only Pe showed a relatively good color. However, the sample stabilized by La(His)₂/Pe with a mass ratio of 0.8:3.2 showed the best initial

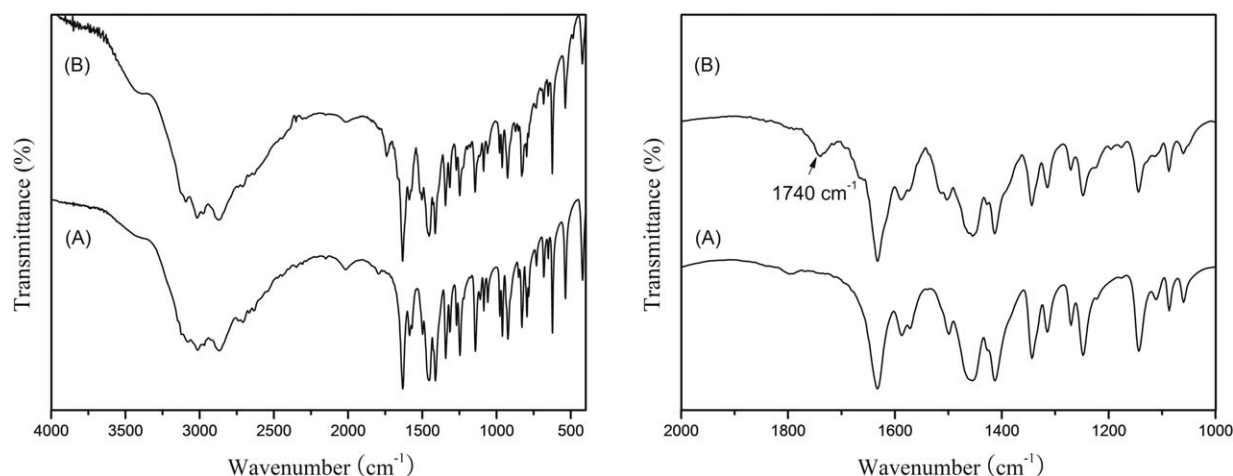


Figure 4. FTIR spectra of the histidine (A) before and (B) after HCl treatment at 180°C for 40 min in the ranges 4000–400 cm^{-1} (left) and 2000–1000 cm^{-1} (right).

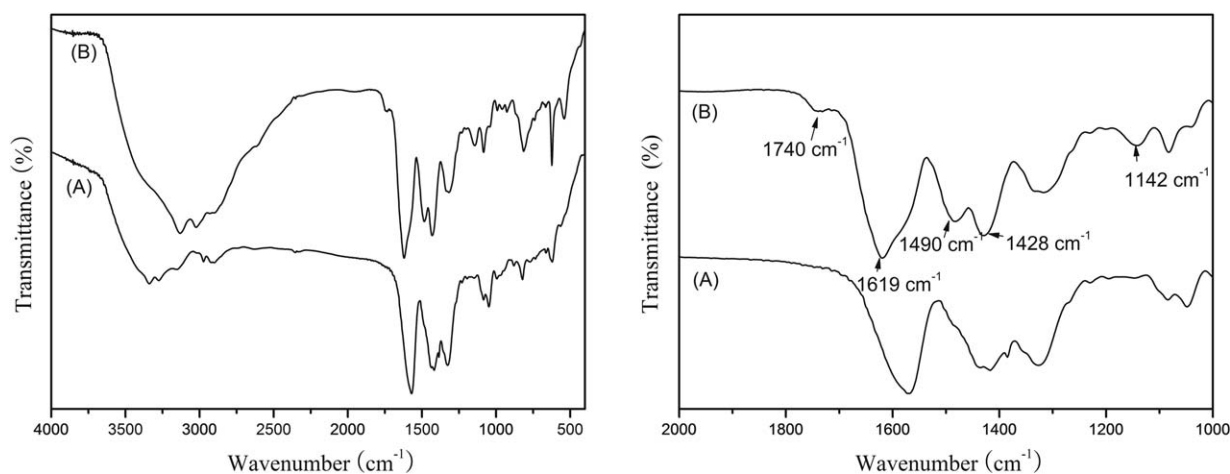


Figure 5. FTIR spectra of $\text{La}(\text{His})_2$ (A) before and (B) after treatment with HCl at 180°C for 40 min in the ranges 4000–400 cm^{-1} (left) and 2000–1000 cm^{-1} (right).

color. From the results of the Congo red test, the stability times of the samples that contained $\text{La}(\text{His})_2$ were longer than that of the sample without $\text{La}(\text{His})_2$. The stability times of the samples increased with increasing $\text{La}(\text{His})_2/\text{Pe}$ ratio.

Pe interacted with the chlorine atom in the PVC chains. The interaction between Pe and chlorine impeded the dehydrochlorination of PVC and the growth of conjugated polyene

Table IV. Stability Times of PVC with $\text{La}(\text{His})_2/\text{Pe}$ for Different Mass Ratios at 180°C

$\text{La}(\text{His})_2/\text{Pe}$ mass ratio	Stability time (min)
4:0	76
3.2:0.8	75
2.4:1.6	70
1.6:2.4	65
0.8:3.2	58
0:4	7

sequences on PVC chain, so the PVC stabilized by Pe had a good initial color.²⁶ However, this interaction was weak, and the functional groups on Pe could not eliminate the generated HCl. Thus, Pe only had a small effect on improving the stability time of PVC in the Congo red test. $\text{La}(\text{His})_2$ eliminated HCl, but it discolored PVC at the same time. When $\text{La}(\text{His})_2/\text{Pe}$ was used with a mass ratio of 0.8:3.2 as a PVC stabilizer, the large amount of Pe retained the initial color of PVC, and the small amount of $\text{La}(\text{His})_2$ stabilized PVC by absorbing the HCl emitted by the degrading PVC without obviously catalyzing the discoloration of PVC. That is why $\text{La}(\text{His})_2/\text{Pe}$ stabilizers with a mass ratio of 0.8:3.2 provided PVC with the best initial color and an acceptable stability time. $\text{La}(\text{His})_2/\text{Pe}$ stabilizers with other mass ratios contained more $\text{La}(\text{His})_2$ and less Pe than those with a mass ratio of 0.8:3.2. The increased use of $\text{La}(\text{His})_2$ in $\text{La}(\text{His})_2/\text{Pe}$ stabilizers with other mass ratios greatly prolonged the stability times of PVC. However, because of the reduced use of Pe and the catalyzing discoloration effect of $\text{La}(\text{His})_2$, the effects of $\text{La}(\text{His})_2/\text{Pe}$ stabilizers with other mass ratios on preventing PVC from discoloration became weak.

Table V. Discoloration of PVC with La(His)₂/Pe for Different Mass Ratios as a Function of the Degradation Time with Heating at 180°C in Air [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

La(His) ₂ /Pe mass ratio	Degradation time (min)						
	0	15	25	35	45	55	65
4:0							
3.2:0.8							
2.4:1.6							
1.6:2.4							
0.8:3.2							
0:4							

PVC, 2.5 g; La(His)₂/Pe, 0.1 g.

That is why La(His)₂/Pe stabilizers with other mass ratios provided PVC with longer stability times but worse initial color than La(His)₂/Pe stabilizers with a mass ratio of 0.8:3.2.

Effects of La(His)₂/Pe/ZnSt₂ on Stabilizing PVC

To further improve the thermal stability of PVC, ZnSt₂ was introduced to stabilize PVC. ZnSt₂ improved the initial color of PVC by replacing the unstable chlorine atoms in the PVC chains with stable stearic groups. However, ZnCl₂ was generated during the stabilizing process and could catalyze complete PVC degradation in a very short time; this is known as *zinc burning*.²⁷ For this reason, ZnSt₂ could only be used with other stabilizers.

The results of the Congo red test and discoloration test of PVC samples containing La(His)₂/Pe/ZnSt₂ with different mass ratios are shown in Tables VI and VII. The results of PbSt₂, as references, are given in Tables VI and VII. The samples stabilized by the La(His)₂/Pe/ZnSt₂ complex showed good thermal stability with both long stability times and good initial color. This result

Table VI. Stability Times of PVC with La(His)₂/Pe/ZnSt₂ for Different Mass Ratios at 180°C

La(His) ₂ /Pe/ZnSt ₂ mass ratio	Stability time (min)
3.2:0:0.8	14
2.4:0.8:0.8	82
1.6:1.6:0.8	88
0.8:2.4:0.8	86
0:3.2:0.8	40
PbSt ₂	94

illustrates that the addition of ZnSt₂ improved the thermal stability of PVC and the color of the samples. Although PbSt₂ provided PVC with the longest stability time and an ideal initial color, the performances of La(His)₂/Pe/ZnSt₂ stabilizers with mass ratios of 0.8:2.4:0.8 and 1.6:1.6:0.8 are promising. La(His)₂/Pe/ZnSt₂ with mass ratios of 0.8:2.4:0.8 produced a color that was lighter than that of PbSt₂ in the 45–65-min duration. As nontoxic stabilizers, La(His)₂/Pe/ZnSt₂ complex stabilizers have the potential to replace PbSt₂ stabilizers.

In a comparison of the results of ZnSt₂/Pe (0.8:3.2) with those of ZnSt₂/La(His)₂ (0.8:3.2), Pe reduced zinc burning more than La(His)₂. The sample stabilized by ZnSt₂/Pe only had half of the stability time compared to those of the samples that contained La(His)₂; this indicated that La(His)₂ prolonged the stability time of PVC greatly, even when the added amount was small. From the previous discussion, the mechanism of the synergistic effect between the components in the La(His)₂/Pe/ZnSt₂ costabilizer is proposed as the following. ZnSt₂ reacted with unstable chlorine atoms in the PVC chains by replacing the unstable chlorine atoms with stable carboxylate groups. Pe acted as an acceptor or a chelating agent for metal chlorides and formed an inert complex with zinc to prevent zinc chloride from catalyzing the degradation of PVC.²⁶ La(His)₂ absorbed HCl released by the degradation of PVC and inhibited HCl from catalyzing the degradation of PVC. Each stabilizing component had an important role in the La(His)₂/Pe/ZnSt₂ costabilizer of synergistically improving the thermal stability of PVC.

CONCLUSIONS

La(His)₂ was prepared from histidine, NaOH, and lanthanum nitrate and was shown to be effective at prolonging the stability time of PVC. La(His)₂ acted as an HCl absorber to prolong the

Table VII. Discoloration of PVC with La(His)₂/Pe/ZnSt₂ for Different Mass Ratios as a Function of the Degradation Time with Heating at 180°C in Air [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

La(His) ₂ /Pe/ZnSt ₂ mass ratio	Degradation time (min)									
	0	15	25	35	45	55	65	75	85	
3.2:0:0.8										
2.4:0.8:0.8										
1.6:1.6:0.8										
0.8:2.4:0.8										
0:3.2:0.8										
PbSt ₂										

PVC, 2.5 g; La(His)₂/Pe/ZnSt₂, 0.1 g.

stability time of PVC. There was a low costabilizing effect on PVC with Pe and La(His)₂; however, the costabilizing effect between La(His)₂, Pe, and ZnSt₂ was excellent. PVCs containing La(His)₂/Pe/ZnSt₂ at mass ratios of 0.8:2.4:0.8 and 1.6:1.6:0.8 exhibited excellent thermal stability with both good initial color and long-term stability with stability times of 86 and 88 min, respectively. The use of only a small amount of La(His)₂ greatly improved the stability times of the costabilizers. Thus, La(His)₂ was a good auxiliary stabilizer. In a future study, we will investigate the costabilizing effect between La(His)₂ and other commercial stabilizers.

ACKNOWLEDGMENTS

This work was financially supported by Natural Science Foundation Program of Inner Mongolia (2015MS0218) and Natural Science Foundation of China (51564040).

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