Insights into the use of zinc-mannitol alkoxide as a novel thermal stabilizer for rigid poly(vinyl chloride)

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ABSTRACT: Zinc–mannitol alkoxide (Zn–Man) was synthesized through alcohol exchange reaction, and investigated by means of Fourier transform infrared spectroscopy and elemental analysis. The thermal stability of Zn–Man for rigid poly(vinyl chloride) (PVC) was evaluated by Congo red testing, conductivity measurements, thermal aging testing, thermogravimetric analysis (TGA), and ultraviolet–visible (UV–vis) spectroscopy test. The experimental results demonstrate that the addition of Zn–Man not only apparently prolonged the static thermal stability time to approximately 96.5 min but also evidently improved the initial color of PVC. More importantly, the color of the PVC sheets stabilized with Zn–Man did not change to black within 180 min; this showed that no zinc-burning phenomenon occurred. In addition, the results of TGA reveal that Zn–Man raised the initial degradation temperature of PVC to about 273.4°C. UV–vis testing indicated that the presence of Zn–Man decreased the content and shortened the length of the conjugated double bonds of PVC. The possible thermal stability mechanism is discussed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42038.
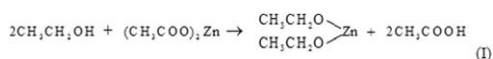
INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used commercial thermoplastics in the world on account of its cost competitiveness and relatively valuable properties, such as its perfect mechanical and physical capacities and its high chemical and abrasion resistance. In particular, therefore, it is used extensively in applications where durability is required.[1] Since its introduction in the early 1950s on a large scale, PVC has taken hold of a prominent position in the construction and medical industries and will continue to hold it in the future.[2] Nevertheless, PVC undergoes severe degradation by dehydrochlorination at its processing temperature; this gives rise to the formation of conjugated double bonds or polyene sequences $[\cdot—(CH=CH)_n—]$, color changes, and consequently, deteriorated properties.[3] Various methods have been tried to solve this problem, among which the addition of different thermal stabilizers is the most efficient and practical, and thus, further degradation is prohibited.[4] During past decades, organic tin, lead salts, metal soaps, and liquid mixed metal stabilizers have been developed and have served as thermal stability additives for PVC.[5] The principal function of these stabilizers is to neutralize the hydrochloric acid (HCl) evolved from the dehydrochlorination reaction of this polymer or replace the unstable chlorine atoms, such as the allyl chlorine atoms in PVC chains.[6,7] Admittedly, organic tin

stabilizers, being relatively new to the market, are of high price and have an unpleasant smell. Lead salts have fairly decent efficiency in stabilizing PVC, but they are the hazardous substances that take a toll on one's health, and more and more restrictions have been imposed. Metal soaps are commonly used stabilizers as well, especially compounded calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$); they play significantly important roles because of their nontoxic attributes. However, an undesirable substance, zinc dichloride ($ZnCl_2$), is produced during the stabilizing process of PVC; in return, it can accelerate the dehydrochlorination of PVC through an autocatalytic effect.[8] The complexity of this formulation of $CaSt_2$/$ZnSt_2$ and the requirement of costabilizers for long-term thermal stability improvement are also drawbacks. Liquid mixed metal stabilizers face the challenge of alleviating the volatilization of organic compounds both in processing and end-use applications.[2]

Given these more or less disadvantages, it is of great necessity to explore a new stabilizer that is nontoxic and can dramatically enhance the thermal stability of PVC. Recently, investigation into polyols as costabilizers has interested many researchers.[9,10] Actually, in previous reports from our research team, pentaerythritol–zinc and pentaerythritol–aluminum served as main stabilizers for rigid PVC, and both of them have shown high efficiency.[11,12] These polyol-based metal alkoxides were inclined

$$2CH_3CH_2OH + (CH_3COO)_2Zn \rightarrow \begin{array}{c} CH_3CH_2O \\ CH_3CH_2O \end{array}\!\!\diagdown\!Zn + 2CH_3COOH$$

(I)

Scheme 1.

Table I. Specific Components of the Prepared PVC Master Batch Without a Stabilizer Before Milling

Component	PVC	ACR	CaCO$_3$	HSt	TiO$_2$	DOP
Mass (g)	100	2	20	1.6	4	5

to absorb HCl, and they were able to react with many active functional groups as well. Therefore, these kinds of metal alkoxides might stand a chance of replacing the labile chlorine of PVC.

With the melting point of 166°C taken into consideration, mannitol is more likely to have perfect compatibility with PVC resin. In this study, zinc–mannitol alkoxide (Zn–Man) was synthesized, and its thermal stabilizing effect on rigid PVC was investigated by means of several experiments. The results indicate that the presence of Zn–Man not only noticeably enhanced the long-term thermal stability of PVC, but it also exhibited an excellent initial color. More importantly, the zinc-burning phenomenon was not observed when Zn–Man was used as a thermal stabilizer for PVC.
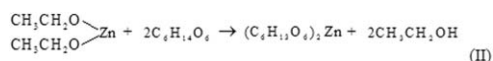
EXPERIMENTAL

Materials

PVC resin (type SG-5, average degree of polymerization is 1005 and viscosity number is 67) from China Petrochemical Qilu Limited Co. (Zibo, China) was used to prepare the samples. CaSt$_2$, ZnSt$_2$, and other thermal additives were kindly supplied by Shandong Huike Additives Co., Ltd. (China). Nanosized zinc acetate was homemade. Mannitol, ethanol, dioctyl phthalate (DOP), calcium carbonate (CaCO$_3$), zinc oxide (ZnO), titanium dioxide (TiO$_2$), ZnCl$_2$, acetic glacial acid, and the other chemicals used were all analytical reagents.

Preparation and Characterization of the Raw Material Zinc Acetate

Glacial acetic acid and ZnO were used to prepare zinc acetate. In the preparation, ZnO (20 g) was slowly added to glacial acetic acid (50 mL) at 80°C. The solution was magnetically stirred until a clear solution was obtained. We obtained a white precipitate by cooling the solution, and the solid product was separated by centrifuging. We washed the precipitate with glacial acetic acid and dried it at 120°C for 3 h. A powdered sample was used, and the particle size was characterized by an FEI Sirion200 scanning electron microscope.

Synthesis and Characterization of Zn–Man

Synthesis of Zn–Man. Homemade zinc acetate (18.35 g) and ethanol absolute (60 mL) were introduced into a round-bottom flask equipped with a water separator. The reaction was carried out at 120°C for 3 h. In this reaction, a faint sour smell was detected. Then, the generated acetic acid and the excess ethanol were distilled off. In the second stage, mannitol (36.44 g) and cyclohexane, working as the carrying agent, were added, and the reaction continued for 2 h at 165°C; magnetically stirring was used throughout the whole process.

$$\begin{array}{c} CH_3CH_2O \\ CH_3CH_2O \end{array}\!\!\diagdown\!Zn + 2C_6H_{14}O_6 \rightarrow (C_6H_{13}O_6)_2Zn + 2CH_3CH_2OH$$

(II)

Scheme 2.

Excess carrying agent was removed by evaporation, and Zn–Man was obtained; it was a white, crispy solid that stuck together in agglomerates. The product was dried and powdered for subsequent use. The reaction equations are represented in Schemes 1 and 2.

Characterization of Zn–Man. Zn–Man was characterized by Fourier transform infrared (FTIR) spectroscopy after it was dried completely. Transmittance was recorded between a wavelength of 400 and 4000 cm^{-1}, with the usual KBr tableting method used, and 32 acquisitions were performed for the sample at a resolution of 4 cm^{-1} with a Nicolet 5700 spectrometer. A blank spectrum was obtained before the measurement to compensate for spectra subtraction resulting from humidity and carbon dioxide in the air.

To determine the structural formula of Zn–Man, elemental analysis and titration were performed. Carbon and hydrogen were analyzed with the help from an outside laboratory with a EuroEA3000 elemental analyzer. Zn–Man was dissolved initially in a 0.5 mol/L HCl solution and was neutralized with ammonia. Then, the content of Zn was quantitatively determined by titration with a standard solution of ethylene diamine tetraacetic acid at pH 5 (sodium acetate and acetic acid buffer were used) with xylenol orange as an indicator. Blank experiment was conducted to eliminate interference. Afterward, the amount of oxygen could be calculated by the difference.

Film Sample Preparation

In the first place, the PVC master batch was prepared by the blending of PVC, stearic acid (HSt), CaCO$_3$, acrylic copolymer (ACR), DOP, and TiO$_2$ intensively in a high-speed mixer for about 2 min. The specific components are shown in Table I. Then, 60 g of the PVC master batch together with different contents of Zn–Man or 4 phr of other additives (including CaSt$_2$/ZnSt$_2$ with a mass ratio of 2:3 and pure mannitol, measured in phr, which indicates the mass ratio of the parts of additives in per hundred grams of PVC resin) were milled, respectively, with an open twin roller for 5 min with the temperature set to 180°C. The thickness of the PVC sheets drawn out was controlled at 1.0 ± 0.1 mm.

Stability Measurements

Congo Red Testing. In accordance with the standard ISO 182-1-1990,[13] the thermal stability time (T_s) could be obtained by the heating of 2.5 g of the PVC sample (by the fragmentation of PVC sheets into about 0.2-mm squares) in a test tube in which the Congo red paper was placed about 2.0 cm over the samples. The test tube was positioned in a glycerol bath, and the temperature was maintained at 180°C. The period of time acquired when the color of the test paper began to change to the point of blue was defined as T_s.
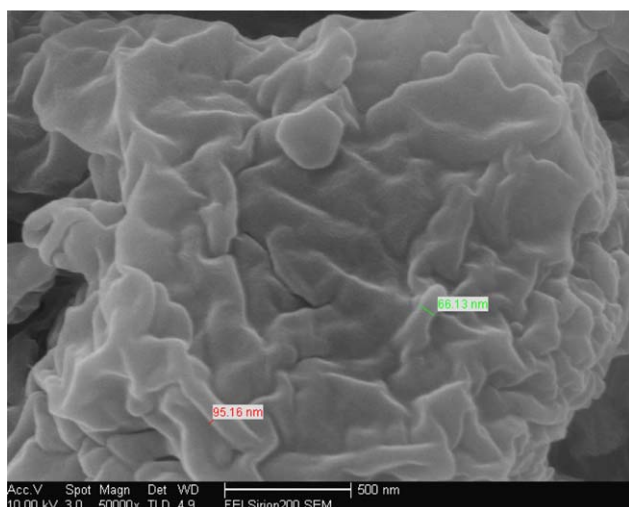
Figure 1. Scanning electron microscopy image of the homemade raw material, zinc acetate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conductivity Measurement. The conductivity measurement was carried out to evaluate the amount of HCl released from the PVC chains when they were heated at 180°C.

The PVC samples were cut into small squares of 2.0 × 2.0 mm^2, with a total weight about 2.0 g each. Later on, one such share was placed into a homemade thermal degradation vessel, and the degradation temperature was set at 180°C. Deionized water was used in the measuring unit, and nitrogen worked as a carrier gas (7.0 L/h). The conductivity of the solution was measured through conductometry.

Thermal Aging Testing. A thermal aging test was performed by the observation of the color evolution of the PVC samples. The PVC sheets were cut into 20 × 20 mm^2 squares; these were heated in a thermal aging test box with forced air convection at 180°C. The operational requirement was in accordance with an ISO standard.[14] These PVC samples were observed at intervals of 10 min.
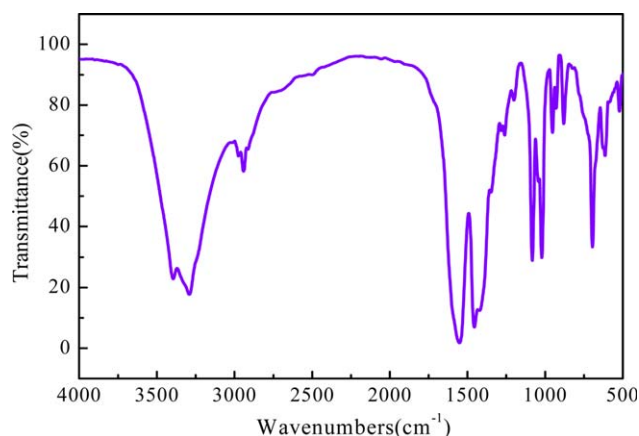

Figure 2. FTIR spectrum of Zn–Man after it was dried completely. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

Thermogravimetric Analysis. The static thermal stability of the PVC resin stabilized with different additives was characterized by TGA with a Shimadzu TGA 50H analyzer under a nitrogen atmosphere (30 mL/min) and heated from 25 to 600°C at a heating rate of 10°C/min, and the weight of the PVC samples used varied in the range of 20–25 mg.

Ultraviolet–Visible (UV–vis) Spectroscopy Testing. UV–vis spectroscopy analysis was adopted to determine the concentration of conjugated double bonds, which were a direct indicator of the degradation situation of the PVC chains.

The optical spectra of PVC samples were recorded on a UV-3600 UV–vis–near-infrared spectrophotometer, and the slit width was set at 2 nm. The wavelength ranged from 200 to 500 nm. Tetrahydrofuran served as the solvent. The temperature used was room temperature.

RESULTS AND DISCUSSION

Morphology of the Homemade Zinc Acetate

The micrograph of zinc acetate is shown in Figure 1. The morphologies of these particles took the form of irregular small rods and discs 95.16 and 66.13 nm, respectively, in size. The particles seemed to be stuck together with each other, as shown in this figure. Smaller sizes of zinc acetate reacted more easily, and these particles exhibited enough chemical properties in the reaction stage.
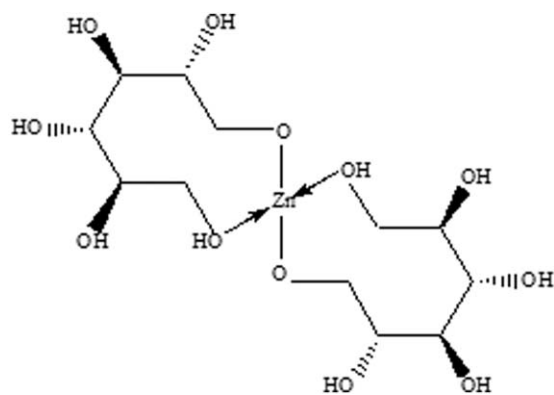
Characterization of Zn–Man

Figure 2 shows the FTIR spectrum of Zn–Man. The peak near 695.8 cm^{-1} was ascribed to the characteristic absorption peak of Zn–O in Zn–Man. The two strong peaks at 3394.9 and 3290.7 cm^{-1} were assigned to the characteristic absorbance of associated —OH, as a result of its stretching vibration. The peak at 2941.3 cm^{-1} belonged to the stretching vibrations of C—H, whereas the peaks at 1551.2 and 1456.1 cm^{-1} were assigned to the bending vibrations of C—H of —C(OH)H— and —CH$_2$—. In addition, the peaks at 1082.6 and 1021.2 cm^{-1} were ascribed to the stretching vibrations of C—O in Zn–Man. Those peaks within 953.3 and 880.9 cm^{-1} belonged to the bending vibrations of C—O and C—C. We inferred that zinc acetate reacted completely with the ethanol molecules; we produced Zn–Man in the second stage after the addition of mannitol because we detected no characteristic absorbances of C=O attributed to the raw material zinc acetate ranging from 1725 to 1700 cm^{-1}.

The results of elemental analysis are listed in Table II. From this table, the experimental formula of the product was $(C_6H_{13.1}O_{6.6})_2Zn_{1.2}$ (with C as the benchmark). It was quite similar to the theoretically calculated $(C_6H_{13}O_6)_2Zn$. The

Table II. Chemical Components of Zn–Man from Elemental Analysis Experiments and Theoretical Calculations

	Reaction product (wt %)			
	C	H	O	Zn
Elemental analysis	30.87	5.63	45.92	17.58
Theoretical calculation	33.71	6.08	44.91	15.30

Scheme 3. Schematic representation of the Zn–Man structure.

Figure 4. Change in the conductivity of an aqueous solution over time for PVC sheets without or with different additives (4 phr) heated at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

product was not likely to be $(CH_3COO)_2Zn$ because the weight percentages of the chemical components were much different than these experimental data.

The analysis of the steric hindrance and reactivity between —OH and active metals, combined with the weight percentages of the chemical components determined through elemental analysis, indicated that the structural formula of $(C_6H_{13}O_6)_2Zn$ that was denoted as Zn–Man was most likely to be like that appearing in Scheme 3.

Appropriate Dosage of Zn–Man

A Congo red test was performed to evaluate the rate of PVC degradation while they were heated at 180°C. The T_s values of the PVC filled with different contents of Zn–Man are presented in Figure 3. They show that the T_s values of the PVC samples stabilized with Zn–Man were significantly improved compared with that of pure PVC. The T_s of pure PVC was just 14.2 min; by contrast, T_s of PVC stabilized with different amounts of Zn–Man was further prolonged, and as a case in point, the T_s value of PVC stabilized with only 1 phr Zn–Man was already 31.6 min. What is more, T_s of PVC increased with increasing dosage of Zn–Man. Nevertheless, along with the increase in Zn–Man,
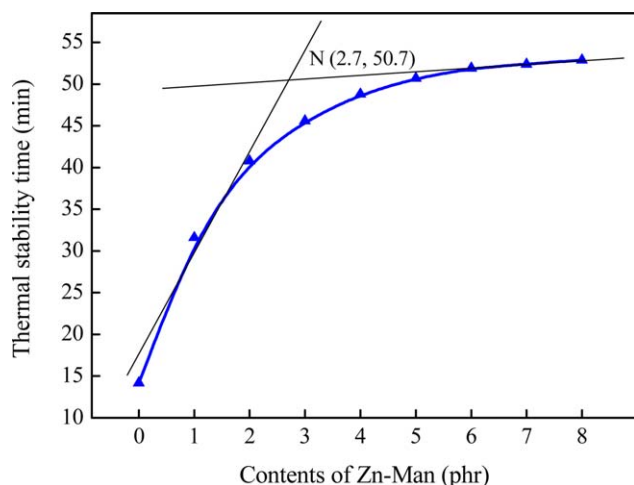

Figure 3. T_s of the PVC samples filled with different amounts of Zn–Man (phr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
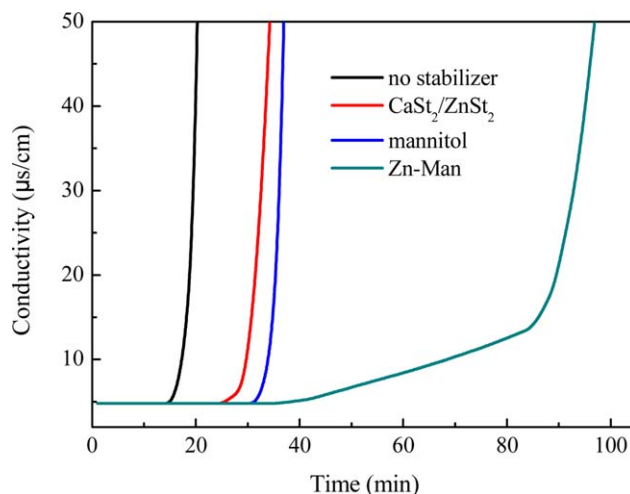
the effect of this improvement on T_s became increasingly insignificant.

Because the presence of Zn–Man prolonged the T_s of the rigid PVC noticeably, it was quite necessary to determine the appropriate dosage, and the starting effect content was defined.[15] The effect of the stabilizers on the T_s values of the PVC samples could be divided into two sections: one characterized with an insignificant effect followed by one that obviously improved T_s. The starting effect content could be obtained graphically from the intersection of the two extrapolations (Figure 3). As shown in Figure 3, the appropriate dosage of Zn–Man was 2.7 phr. This showed that a desirable thermal stabilizing effect was achieved when the content of Zn–Man was 2.7 phr. However, the dosage of commercial thermal stabilizers was usually 4 phr. To compare the thermal stabilization performance, the dosage of Zn–Man taken was also 4 phr.

Conductivity Measurement

Generally speaking, in the process of heating, the degradation of PVC primarily involves a progressive unzipping of neighboring labile chloride atoms,[15] and then, HCl is released. The conductivity measurement was conducted to quantitatively evaluate the amount of evolved HCl gas, whereas the PVC samples were heated at 180°C.

The period from the beginning of heating to the point when the conductivity started to increase was defined as the induction time, whereas the period thereafter up to the point where the conductivity value reached 50 $\mu s/cm$ was ΔT. The whole time span was called the *stability time,* which was seen as the maximum acceptable level of thermal decomposition of PVC. ΔT is able to reflect the effects of a thermal stabilizer for inhibiting the formation of HCl or absorbing the HCl molecules produced after the PVC samples were heated for a certain period of time. In the form of contrast, the pure PVC and PVC stabilized with $CaSt_2/ZnSt_2$, mannitol, and 4 phr Zn–Man were tested, respectively, and the results are presented in Figure 4. Visually, the

Table III. Color Evolution of the PVC Sheets Mixed with No Stabilizer or Different Additives and Treated at 180°C for Different Periods of Time. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

| Additives	Thermal aging degradation time (×10 minutes)											
	0	1	2	3	4	5	6	8	10	12	15	18
No stabilizer												
CaSt₂/ZnSt₂												
Mannitol												
Zn-Man												

induction time, stability time, and ΔT could be read from these curves, which depict the changes in the conductivity, which was a function of time.

Figure 4 provides a direct visual description of the pyrolytic status of PVC when it was heated at 180°C. The longest stability time (96.5 min) and induction time (37.2 min) of the PVC samples stabilized with 4-phr Zn–Man demonstrated that Zn–Man had an excellent stabilizing effect on the rigid PVC. This could be ascribed to the excellent effect of Zn–Man for neutralizing HCl or inhibiting HCl from being produced. However, CaSt₂/ZnSt₂, a widely used stabilizer, exhibited a much shorter induction time and stability time because of ZnCl₂ produced in the thermal stabilizing process, which could catalyze the dehydrochlorination reaction of PVC. A little longer T_s of PVC with pure mannitol compared with that of PVC with CaSt₂/ZnSt₂ also complied with the conclusion from some published reports

that a range of polyols alone have certain inhibiting effects on the thermal degradation of PVC. Thus, the result that mannitol exhibited some thermal stabilizing effects on PVC could be interpreted as follows: that the presence of mannitol could react with the produced HCl to form a certain complex, which could seriously constrain autocatalytic degradation.[16] On the other hand, the much longer T_s of PVC with Zn–Man compared with that of PVC with mannitol demonstrated that the product obtained from the reaction of zinc acetate and mannitol had new structure, which was able to improve the thermal stability of PVC.

Thermal Aging Test

To assess the color stability of PVC stabilized with different stabilizers, a thermal aging test was conducted correspondingly. The discoloration of the PVC sheets was the consequence of polymer dehydrochlorination; that is, the color was
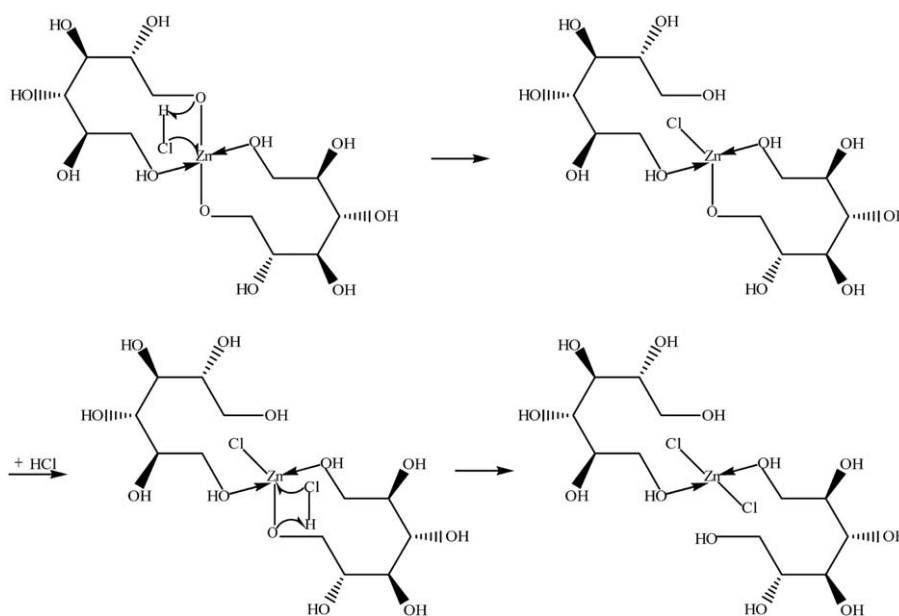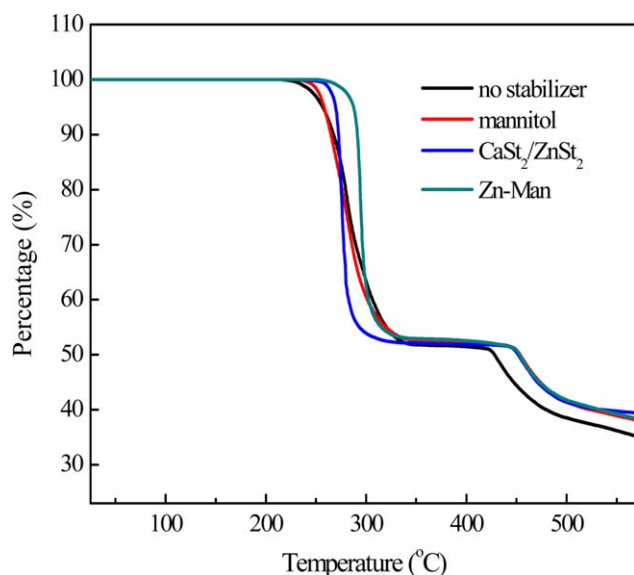

Scheme 4.

Figure 5. Curves of TGA for PVC without or with different additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. UV–vis spectra of PVC stabilized with no stabilizer or different additives and heated at 180°C for 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decided by those conjugated double bonds, which were generated while the PVC sheets were heated and whose length was no less than a certain numeric. The more conjugated double bonds there were, the darker the coloration was. Table III shows the color evolution of PVC stabilized with different additives treated at 180°C as a function of the time.

As is shown in Table III, PVC containing Zn–Man exhibited not only excellent initial color but also long-term thermal stability. The color of PVC stabilized with Zn–Man did not change to black within 180 min. Compared with other additives, Zn–Man showed a super effect on maintaining the color stability of rigid PVC. As a matter of fact, the color of pure PVC began to change even during the milling process with the open twin-roller within 5 min, and it totally turned black after 30 min. In addition, Table III shows that
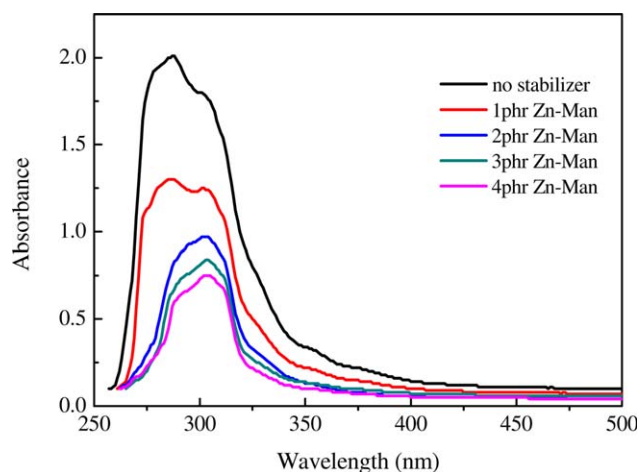
PVC sheets stabilized with Zn–Man and $CaSt_2/ZnSt_2$ both had excellent initial color within the initial 20 min. However, the color of PVC having $CaSt_2/ZnSt_2$ started to darken after 20–30 min, and it turned entirely black after 40 min. This was attributed to the fact that it was easy for the PVC samples stabilized with $CaSt_2/ZnSt_2$ to emerge the zinc-burning phenomenon. In the course of heating, $ZnSt_2$ could react with the HCl released from PVC degradation to form $ZnCl_2$, which as a strong Lewis acid, might have catalyzed the decomposition of PVC and caused abrupt blackening. As for the mannitol system, the initial color was better than that of pure PVC, and it exhibited limited thermal stability as well. Black dots emerged on the edge of the PVC sheets stabilized with mannitol within 40 min, and the color changed to completely black within the subsequent 10 min. We hold the opinion that this serious decomposition resulted from the absence of a certain compound, which was capable of preventing PVC from degrading. That is, although mannitol might have inactivated labile chlorine atoms to a certain extent to improve

Figure 6. UV–vis spectra of PVC stabilized with no stabilizer or with different amounts of Zn–Man heated at 180°C for 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
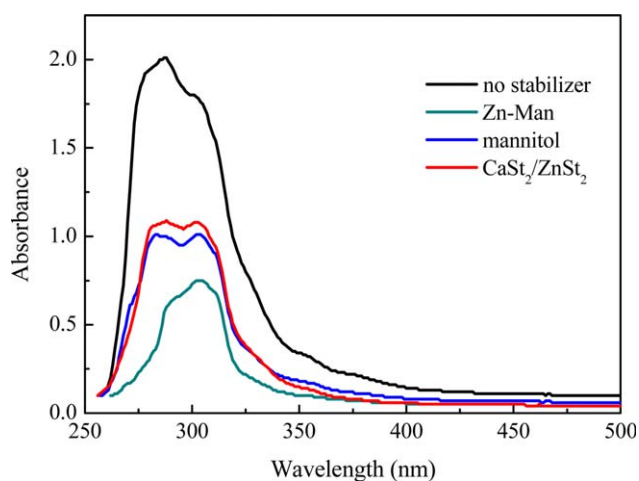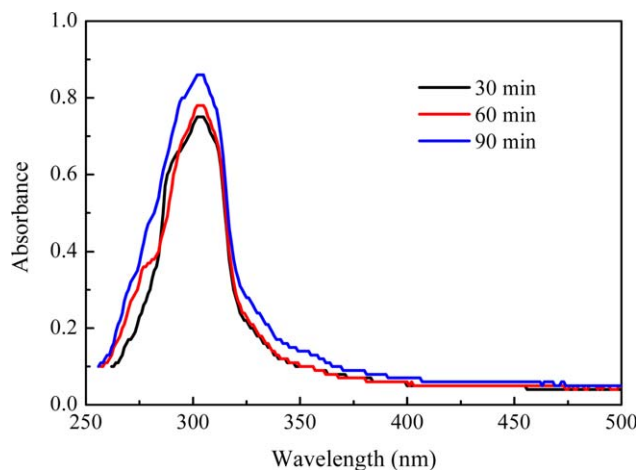

Figure 8. UV–vis spectra of PVC stabilized with 4-phr Zn–Man and heated at 180°C for different times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. HCl Absorption Capacity of Several PVC Thermal Stabilizers

Stabilizer	mg of HCl/g of additive
Lead salt	277.8
CaSt$_2$	104.6
ZnSt$_2$	93.7
Zn–Man	53.2

the initial color, it did not possess the ability to absorb the released HCl and prolong the long-term thermal stability of PVC.

Actually, this detrimentally autocatalytic degradation phenomenon[1,8,17] was not observed in PVC stabilized with Zn–Man within 180 min. The possible reason was that there was no free ZnCl$_2$ produced in the degradation of the PVC stabilized with Zn–Man, as illustrated in reaction III in Scheme 4, and thus, no catalytic effect of ZnCl$_2$ was observed. In view of its effects on

the initial color and long-term thermal stability, Zn–Man showed effects on the thermal stability for rigid PVC. The mechanism of Zn–Man is discussed in the Thermal Stabilizing Mechanism of Zn–Man on PVC section.

TGA

Figure 5 shows the dynamic thermogravimetric curves of the PVC samples stabilized with different thermal stabilizers. According to Figure 5, there existed two distinct weight loss stages: the first stage was attributed to dehydrochlorination followed by the formation of conjugated polyene sequences, and the second one corresponded to the thermal cracking of carbonaceous conjugated polyene sequences to low-molecular-weight hydrocarbons and the generation of carbonaceous residues.[18] Therefore, only the first stage was under discussion, and the temperature was in the range 25–375°C.

As shown in Figure 5, the addition of Zn–Man caused the initial degradation temperature (T_i; the corresponding temperature when the mass loss percentage of PVC was 1%) of the PVC
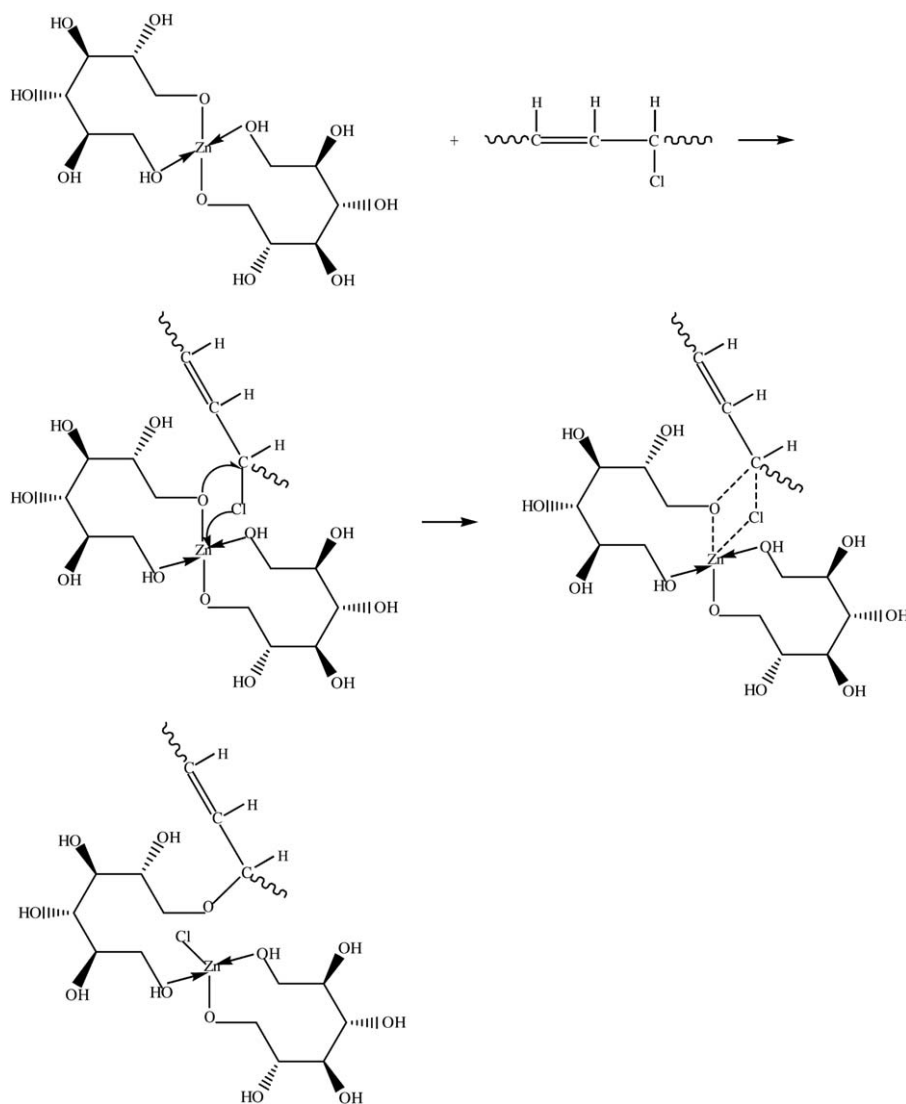

Scheme 5.

Table V. Color Evolution of PVC Sheets Compounded with Different Ratios of $ZnCl_2$ to Zn–Man and Heated at 180°C for Different Periods of Time. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ratios of $ZnCl_2$ and Zn-Man	Thermal aging degradation time (×10 minutes)											
	0	1	2	3	4	5	6	8	10	12	15	18
0:0												
4:0												
2:2												
0:4												

samples to increase from 233.9 to 273.4°C. This was higher than that of the PVC samples stabilized with $CaSt_2/ZnSt_2$ or mannitol. T_i may have reflected the complexity of the dehydrochlorination of PVC. The higher T_i was, the harder it was for the PVC chains to take off HCl. Zn–Man exhibited an excellent effect on inhibiting the dehydrochlorination of PVC.

UV–Vis Spectroscopy Analysis

It is well known that the UV–vis spectrum shows the length of conjugated carbon chains, whereas the absorption intensity is related to the concentration of conjugated double bonds.[19] Therefore, the results of UV–vis spectroscopy was used to investigate the status of the thermal degradation of PVC.

Figure 6 presents the UV–vis spectra of the pure PVC and PVC stabilized with different contents of Zn–Man heated at 180°C for 30 min. It shows that the absorbance of PVC stabilized with different amounts of Zn–Man were all less than that of the pure PVC; this demonstrated that the addition of Zn–Man decreased the content of conjugated double bonds of PVC. The concentration of conjugated double bonds decreased obviously with an increase in the amount of Zn–Man. Furthermore, the decline of the absorption intensity became more and more indistinctive when the dosage of Zn–Man exceeded 2 phr. This also demonstrated the fact that the appropriate dosage of Zn–Man was about 3 phr.

Figure 7 represents the UV–vis spectra of the pure PVC and PVC stabilized with different stabilizers heated at 180°C for 30 min. Figure 7 shows that the peak height of PVC stabilized with Zn–Man was the lowest of the four PVC samples. This indicated that Zn–Man had a better thermal stabilizing effect on PVC than the $CaSt_2/ZnSt_2$ and mannitol. Figure 8 depicts the UV–vis spectra of PVC stabilized with 4-phr Zn–Man heated at 180°C for different periods of time. Figure 8 indicates that the absorbance of PVC samples heated for 90 min increased a little compared with that for 30 min; this demonstrated that Zn–Man was effective enough to postpone the degradation of PVC when heated.

Thermal Stabilizing Mechanism of Zn–Man on PVC

Capacity for Absorbing HCl. Metal alkoxides are strong alkalis and good nucleophilic reagents. They are powerful for neutralizing HCl. Unfortunately, the easy hydrolyzation of metal alkoxide makes them unsuitable for use as thermal stabilizers for PVC. However, Zn–Man, a polyol-based metal alkoxide, is not easy to hydrolyze, and it can be used as a thermal stabilizer for PVC. As a thermal stabilizer, one of the main functions of Zn–Man is to neutralize the HCl produced. In an attempt to reveal the exact mechanism of Zn–Man, a titration experiment was conducted. A certain volume of 0.1 mol/L HCl was used to dissolve quantitative Zn–Man, $CaSt_2$, $ZnSt_2$, and lead salts, and then, the excessive HCl was determined by a 0.1 mol/L NaOH solution through the back acid–base titration method. Thus, the ability to neutralize the HCl of these additives was calculated. Table IV lists the results.

Table IV shows that the ability of Zn–Man to neutralize HCl was not as strong as that of lead salts, $ZnSt_2$, and $CaSt_2$. Another main function of Zn–Man in stabilizing PVC could be the formation of coordinative bonds with the allyl chloride atoms of PVC because of the good coordination effect of Zn. The UV–vis absorption spectrum in Figure 7 shows that the absorbance significantly decreased with the addition of Zn–Man. This indicated that the concentration of conjugated double bonds decreased dramatically; this showed that Zn–Man could substitute for the labile chlorine atoms of PVC, and the further formation of the conjugated double bonds was suppressed. Moreover, the oxygen atoms of the alkoxy groups of Zn–Man had a low negative charge, and zinc atoms had a high positive charge. Just like the $ZnSt_2$, Zn–Man could displace the allyl chloride atoms of PVC to form a stable structure (reaction IV in Scheme 5). This showed that PVC with Zn–Man alone exhibited a good initial color.

Effect of Zn–Man on Chelation of $ZnCl_2$

As is generally known, $ZnCl_2$, which is a strong Lewis acid acting as an autocatalyst,[11] is a generated substance that can, in return, exacerbate the degradation of PVC in its heating process. As shown in Table III, the zinc-burning phenomenon did not happen to the PVC samples stabilized with Zn–Man within 180 min when heated at 180°C. With the purpose of verifying the effect of Zn–Man to chelate $ZnCl_2$, pure $ZnCl_2$ and the mixture

of Zn–Man/ZnCl$_2$ were used as thermal stabilizers for PVC. The thermal stability of PVC sheets stabilized with pure ZnCl$_2$ and Zn–Man/ZnCl$_2$ was tested with the thermal aging test, and Table V shows the results.

As demonstrated in Table V, the PVC sheets with pure ZnCl$_2$ turned completely black within 10 min. This phenomenon indicated that the existence of ZnCl$_2$ indeed accelerated the degradation of PVC and caused serious zinc burning. By contrast, when the ratio of Zn–Man/ZnCl$_2$ was 2:2, the PVC sheets became totally black after they were heated for 60 min. This demonstrated that hydroxyl of Zn–Man could form complexes with ZnCl$_2$ to prevent the zinc-burning phenomenon.

The reason that Zn–Man possessed significantly excellent long-term thermal stability was likely that this alkoxide functioned like this: Zn–Man could substitute for the labile chlorine atoms of the PVC chains in the first place (reaction IV, mainly the allyl chloride atoms). Then, no zinc chloride, which could accelerate the degradation of PVC, was produced in the neutralization reaction. Therefore, PVC stabilized with Zn–Man solely could gain long-term stability, as could be seen from the results of the experiment.

CONCLUSIONS

Zn–Man was synthesized through an alcohol-exchange reaction, and its structural formula was confirmed. The thermal stability tests showed that PVC containing Zn–Man exhibited not only excellent original color but also long-term thermal stability. The thermal stability mechanism of Zn–Man was investigated. The excellent thermal stabilizing performance could be attributed to the strong coordination of zinc atoms in Zn–Man with active chloride atoms in PVC chains, such as allyl chloride, and the medium ability to neutralize HCl. More importantly, Zn–Man had a strong effect on the formation of complexes with ZnCl$_2$. Therefore, no free ZnCl$_2$ could be released during the process of the thermal stabilization of PVC, and no zinc burning was observed.

However, Zn–Man could be more effective as a thermal stabilizer. In experiments, the compatibility between this alkoxide and PVC was not that ideal, which limited its effects. If its melting point could be reduced, it might perform better.

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REFERENCES

1. Li, D.; Zhou, M.; Xie, L.; Yu, X.; Yu, Y.; Ai, H.; Tang, S. *Polym. J.* **2012**, *45*, 775.

2. Wallenwein, G. *Plast. Additives Compd.* **2006**, *8*, 26.

3. Tawfik, S. Y.; Asaad, J. N.; Sabaa, M. W. *Polym. Degrad. Stab.* **2006**, *91*, 385.

4. Zhu, X.; Song, Y.; Zheng, Q. *J. Appl. Polym. Sci.* **2012**, *126*, 980.

5. Liu, J.; Shang, H.; Zheng, Y.; Song, X. *J. Appl. Polym. Sci.* **2009**, *113*, 12162.

6. Starnes, W. H., Jr. *Polym. Degrad. Stab.* **2012**, *97*, 18151.

7. Xu, X.; Chen, S.; Tang, W.; Qu, Y.; Wang, X. *Polym. Degrad. Stab.* **2014**, *99*, 211.

8. Manzoor, W.; Yousaf, S. M.; Ahmad, Z. *Polym. Degrad. Stab.* **1996**, *51*, 295.

9. Steenwijk, J.; Langerock, R.; van Es, D. S.; van Haveren, J.; Geus, J. W.; Jenneskens, L. W. *Polym. Degrad. Stab.* **2006**, *91*, 52.

10. Benavides, R.; Edge, M.; Allen, N. S.; Tellez, M. M. *J. Appl. Polym. Sci.* **1998**, *68*, 11.

11. Xu, S.; Li, D.; Yu, X.; Zhang, Y.; Yu, Y.; Zhou, M.; Tang, S. *J. Appl. Polym. Sci.* **2012**, *126*, 569.

12. Xie, L.; Li, D.; Zhang, J. *J. Appl. Polym. Sci.* **2013**, *130*, 37049.

13. Plastics; Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures; Part 1: Congo red method; ISO 182-1-1990; International Organization for Standardization: Geneva, Switzerland, **1990**.

14. Plastics; Determination of thermal stability of poly(vinyl chloride), related chlorine-containing homopolymers and copolymers and their compounds; discoloration method; ISO 305-1990(E); International Organization for Standardization: Geneva, Switzerland, **1990**.

15. Wang, M.; Xu, J.; Wu, H.; Guo, S. *Polym. Degrad. Stab.* **2006**, *91*, 21019.

16. Steenwijk, J.; Van Es, D. S.; Van Haveren, J.; Geus, J. W.; Jenneskens, L. W. *Polym. Degrad. Stab.* **2006**, *91*, 22330.

17. Sombatsompop, N.; Sungsanit, K.; Thongpin, C. *Polym. Eng. Sci.* **2004**, *44*, 487.

18. Pappa, A.; Mikedi, K.; Agapiou, A.; Karma, S.; Pallis, G. C.; Statheropoulos, M.; Burke, M. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 106.

19. Zhang, Q.; Li, H. *Spectrochim Acta A* **2008**, *69*, 62.