Synthesis and Study of Zinc Orotate and Its Synergistic Effect with Commercial Stabilizers for Stabilizing Poly(Vinyl Chloride)

Feng Ye 1,*, Qiufeng Ye 2, Haihua Zhan 1, Yeqian Ge 1, Xiaotao Ma 1, Yingying Xu 1 and Xu Wang 3

1 College of Textile and Garment, Shaoxing University, Shaoxing 312000, China; zhb@usx.edu.cn (H.Z.); geyeqian@163.com (Y.G.); mxt775382687@163.com (X.M.); 18868914618@163.com (Y.X.)
2 Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Zhejiang 315000, China; yeqifeng@nimte.ac.cn
3 College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou 310014, China; wangxu@zjut.edu.cn

* Correspondence: yefeng@usx.edu.cn; Tel.: +86-18767191283

Received: 6 January 2019; Accepted: 21 January 2019; Published: 23 January 2019

Abstract: Zinc orotate (ZnOr2), which is a new kind of poly(vinyl chloride) (PVC) stabilizer, is prepared in this work through the precipitation method, and its impact on the thermal stability of PVC is measured by thermogravimetric analysis (TG), Congo red test, and discoloration test. The results exhibit that the thermal stability of PVC is positively enhanced after the addition of ZnOr2. In contrast with a commercial thermal stabilizer, zinc stearate (ZnSt2), a noteworthy improvement was observed that ZnOr2 could postpone the “zinc burning” of PVC. This is principally ascribed to the Or anion in the structure of ZnOr2 being able to absorb the HCl released by PVC, and to supersede unstable chlorine atoms in the structure of PVC. In addition, blending ZnOr2 with calcium stearate (CaSt2) in diverse mass ratios can significantly accelerate the thermal stability of PVC. Optimum performance was achieved with a CaSt2:ZnOr2 ratio of 1.8:1.2. Moreover, an outstanding synergistic effect can be observed when CaSt2/ZnOr2 is coupled with other commercial auxiliary stabilizers. The initial color and long-term stability of PVC including CaSt2/ZnOr2 is significantly increased when pentaerythritol (PER) is added, while dibenzoylmethane (DBM) can only improve its long-term thermal stability.

Keywords: poly(vinyl chloride); zinc orotate; dibenzoylmethane; thermal stabilizer; pentaerythritol; synergistic effect

1. Introduction

Poly(vinyl chloride) (PVC) is a kind of thermoplastic polymer manufactured by the polymerization of vinyl chloride monomer. It has extensive applications in the living and industrial fields because of its advantages for mature production technology, easy to process molding, corrosion resistance, abrasion resistance, flame retardant properties, and good electrical insulating performance [1–3]. However, the HCl can be easily removed from the structure of PVC, because the molecule contains allylic and tertiary chlorine atoms. The HCl will then further catalyze the degradation of PVC, resulting in the product gradually converting from white to completely black [4–6]. Therefore, thermal stabilizers should be added to PVC to prevent its degradation.

Over the past few decades, various compounds have been studied as PVC stabilizers, such as metal soaps [7], lead salts [8], and organotin [9–11]. Although lead salts and organotin have been shown to be highly effective in stabilizing PVC, the properties of high toxicity for lead salts and high price for
organotin limit their application [9–11]. On the other hand, metal soaps are also restricted because of their low workpiece ratio. Therefore, it is urgently necessary to discover environmentally friendly and efficient thermal stabilizers. Recently, calcium/zinc thermal stabilizer (Ca/Zn), as one of the most commonly used metal soap stabilizers, has been playing an important role in this field due to its low toxicity [12,13]. However, an undesired product formed from Ca/Zn in PVC is zinc chloride (ZnCl₂), which may accelerate the degradation of PVC and lead to a sudden “zipper dehydrochlorination” attributed to its strong Lewis acidity, so it can produce the “zinc burning” phenomenon [14]. Therefore, researchers have spent a considerable amount of time seeking a new zinc stabilizer that has no active catalytic effect on degrading PVC. Huanzhang Chen and co-workers synthesized zinc cyanurate under weak acid conditions, and investigated its thermal stability when combined with PVC. It was found that zinc cyanurate was superior to traditional zinc stearate [15]. Xu Wang and co-workers investigated the synergistic effect between zinc cyanurate and calcium stearate on the thermal stability of PVC [16]. Baoqing Shentu and co-workers researched the synthesis of zinc mannitol and its potency to stabilize PVC [17]. It was found that zinc mannitol could significantly enhance the thermal stability of PVC. Shumin Li and Youwei Yao studied the synthesis of zinc barbiturate, which showed good efficiency and synergistic effects on the thermal stability of PVC [18].

On the other hand, Starnes and co-workers carried out a large number of experiments to investigate pyrimidine diketone derivatives as PVC thermal stabilizers [19]. These compounds exhibited thermal stability for PVC, and some have been applied for industrial products. Simultaneously, Santamaria and co-workers also reported pyrimidine compounds as thermal stabilizers for PVC, and investigated the mechanism of thermal stability process [20]. It was found that pyrimidinedione derivatives could replace labile chlorines by N-alkylation reaction and stop the growth of polyene sequences in PVC chains. Therefore, we deduce that the presence of pyrimidine diketone structures in the compounds had an active effect in stabilizing PVC. In this article, we consider the structural resemblance of orotic acid (Or) to pyrimidinedione. The target of this work is to research the possibility of using zinc orotate (Zn(C₅H₃N₂O₄)₂, abbreviated as ZnOr₂) as a new thermal stabilizer for PVC.

2. Materials and Methods

2.1. Materials

PVC (SG-5, polymerization temperature: 55 °C, average degree of polymerization: 1000) applied in this work was acquired from Xinjiang Tianye (Group) Co. Ltd., Shihezi, China. Calcium stearate (CaSt₂, calcium content: 6.6–7.4%), zinc stearate (ZnSt₂, zinc content: 10–12%), and calcium carbonate (CaCO₃, 1000 mesd) were acquired from Zhejiang Himpton New Material Co. Ltd., Hangzhou, China. Ca/Zn thermal stabilizers (Ca/Zn) were included in the form of CaSt₂ (50 wt %) and ZnSt₂ (50 wt %). Dioctyl phthalate (DOP, 98%), orotic acid (Or) (AR, 98%), zinc acetate (AR, 99%), dibenzoylmethane (DBM, AR), and pentaerythritol (PER, AR) were acquired from Aladdin Reagent., Shanghai, China. Other chemical reagents used in this study were analytical reagents.

2.2. Preparation and Characterization of ZnOr₂

ZnOr₂ was prepared on the basis of the following process: Or (1.74 g, 10 mmol) and sodium hydroxide (0.4 g, 10 mmol) were mixed in a 100 mL three-neck flask with a magnetic drive stirrer, a condenser, and a dropping funnel. Next, 20 mL distilled water was added to clarify while stirring at room temperature. After dissolving zinc acetate (2.20 g, 10 mmol) with 15 mL of distilled water, the zinc acetate solution was slowly dripped into the Or solution. After all had been added, the mixed solution was reacted for 1 h at 85 °C. The filtrate was removed by extraction filtration and subsequently washed three times with distilled water. Finally, the white solid (ZnOr₂) was dried in the oven at 180 °C, and the yield was 78.6%. The synthesis pathway of ZnOr₂ is shown in Scheme 1.
Scheme 1. Synthesis pathway of ZnOr2.

The ZnOr2 was measured using an elemental analyzer (Euro EA 3000, EA Instruments, Milan, Italy) to determine the content of carbon, hydrogen, and nitrogen in ZnOr2. The zinc content of ZnOr2 was ascertained using the crucible process. The molecular structure of the sample was ascertained through Fourier transform infrared (IRPrestige-21, Shimadzu Corp., Kyoto, Japan) in the range of 4000–400 cm\(^{-1}\) with a KBr disc. The thermogravimetric curve was confirmed through thermogravimetric analyzer (TG/DTA6300, Seiko Instruments Inc., Chiba, Japan) in an air atmosphere, with temperature increasing from 25 to 800 °C at a heating rate of 10 °C/min.

2.3. Preparation of PVC Samples

Mixtures containing PVC powder resin (50 phr), PVC paste resin (50 phr), DOP (50 phr), CaCO3 (15 phr), and stabilizers (3 phr) were mixed in a beaker. After being stirred to homogeneity, the mixtures were poured into a glass mold with a thickness of 1.0 mm to plasticize for 40 min at the temperature of 140 °C. After the plasticization was completed, the mixture was cooled slightly and cut with an engraving knife to the proper size (15.0 mm \( \times \) 20.0 mm \( \times \) 1.0 mm).

2.4. Evaluation of Stabilizing Efficiency

2.4.1. Congo Red Test

The PVC powder was ground and mixed with 3 phr thermal stabilizers in a mortar. Next, the Congo red test paper was placed in a glass tube containing the sample. The distance between the Congo red test paper and the PVC sample was 20 mm. The static thermal stability of the PVC sample was evaluated by immersing the glass tube in an oil bath at 180 °C. The static thermal stability time (T\(_s\)) is defined as the time when the Congo red paper begins to turn blue. Congo red tests were carried out three times to accurately calculate the mean value of thermal stability time.

2.4.2. Discoloration Test

PVC slices with approximately 1.0 mm thickness were cut to size, about 15.0 mm \( \times \) 20.0 mm. They were then placed on an aluminum foil paper and shifted to a temperature-controlled ageing oven (UF260, Memmert Inc., Schwabach, Germany). The PVC sheets were heated at 180 °C. PVC sheets were removed from the ageing oven every 10 min and scanned with a scanner (LiDE120, Canon Inc., Tokyo, Japan). The effect of the thermal stabilizer on the PVC can be compared through the color change of the heated PVC sheets.

2.4.3. Thermogravimetric Analysis

Thermal degradation of the stabilized PVC samples was tested on a thermogravimetric analyzer (TG/DTA6300, Seiko Instruments Inc., Chiba, Japan) from room temperature to 800 °C at a heating rate of 10 °C/min, in an air atmosphere.

2.4.4. Investigation of the Mechanism of ZnOr2 for Stabilizing PVC

The subjacent two experiments were carried out to investigate the pattern of behavior of ZnOr2 as a thermal stabilizer for stabilizing PVC \[16,21\].
A certain amount of ZnOr$_2$ was added to a three-necked flask and then heated to 180 °C in the oil bath. After being subjected to a steady flow of dry HCl gas for 2 h, the sample was subsequently heated to 120 °C in air for 4 h to get rid of the remaining HCl gas. The treated product was put into the deionized water and then filtered to remove filter residue. Finally, one drop of 0.1 mol/L silver nitrate solution was added to ascertain whether the filtrate included chloride ions. This experiment could ultimately demonstrate whether ZnOr$_2$ can be taken as an HCl absorber.

Another experiment was conducted to explore whether ZnOr$_2$ could supersede unstable chlorine atoms in PVC chains. A certain amount of ZnOr$_2$ and PVC powder were ground and mixed in a mortar, and subsequently mixed in an open twin-wheel mill for 10 min at 180 °C. After mixing was completed, the PVC containing ZnOr$_2$ was dissolved in tetrahydrofuran and filtered to get rid of the unreacted ZnOr$_2$. Finally, the PVC samples were precipitated with methanol and gathered by filtration. The purified samples were aged at different time intervals (0–40 min) at 180 °C in air, and characterized by FTIR spectroscopy (IRPrestige-21, Shimadzu Corp., Kyoto, Japan).

3. Results

3.1. Characterization of ZnOr$_2$

Or is an organic acid, so it is understood that the ZnOr$_2$ synthesized in neutral conditions in our lab is an organic salt. The elemental analysis results of ZnOr$_2$ revealed that the atomic concentration proportion of zinc to nitrogen was about 1:4. And the zinc content of ZnOr$_2$ acquired by heat weight of the crucible was 15.68 %. Therefore, we infer that the molecular formula of this compound is Zn(C$_5$H$_3$N$_2$O$_4$)$_2$·2H$_2$O (theoretical value of zinc content is 15.82%) \[22,23\].

In this article, ZnOr$_2$ is used to represent Zn(C$_5$H$_3$N$_2$O$_4$)$_2$·2H$_2$O. The thermal action of ZnOr$_2$ was characterized by TGA at heating rate of 10 °C/min. As shown in Figure 1, the TGA curve of ZnOr$_2$ reveals an estimated mass loss of 8.9% at the temperature range from 25 to 300 °C, which was assigned to the absorbed water. This result also proved that there are two absorbed water molecules in ZnOr$_2$ \[24,25\].

![Figure 1. The TGA and DTG curves of ZnOr$_2$ from room temperature to 800 °C at a heating rate of 10 °C/min in an air atmosphere.](image)

It can also be observed from the curve that further disintegration of ZnOr$_2$ occurred over 300 °C, which can be broken down into two stages. The first thermal weight loss stage occurred with an approximate mass loss of 64.9% (calculated 63.1%) at a temperature extent of 300–420 °C, which is mainly attributed to the release of three carbon monoxide molecules. The second mass loss stage of 8.42%, which occurred at the temperature extent of 490–800 °C, can be attributed to the decomposition of remnant cyanurate anions, and finally left the ZnO residue at 18.4% (calculated 19.71%). On the other hand, the TGA curve also suggests that ZnOr$_2$ has very little weight loss when the temperature
is dropped to 200 °C. Therefore, ZnOr$_2$ is stable within the processing temperature of PVC systems, in the range of 160–200 °C.

The Fourier transform infrared (FTIR) spectra of ZnOr$_2$ and Or are shown in Figure 2. As shown in Figure 2, it can be observed that the stretching vibration peak and symmetric stretching vibration peak of COOH for Or were transferred from 3515.4 and 1271.6 cm$^{-1}$ to 3415.8 and 1373.9 cm$^{-1}$, respectively, after generating Zinc salts. It can also be ascertained that ZnOr$_2$ has been successfully synthesized [26,27].

![Figure 2. The Fourier transform infrared (FTIR) spectra of Or and ZnOr$_2$.](image)

**3.2. Thermal Stability of ZnOr$_2$ Stabilized PVC**

Figure 3 shows the Congo red test results of PVC samples containing various thermal stabilizers [26,27]. From the figure, it can be observed that the thermal stability time of pure PVC is about 390 s. After addition of the ZnOr$_2$ and Ca/Zn thermal stabilizers, the thermal stability times of PVC samples were increased to 500 s and 490 s, respectively. The results indicate that PVC samples stabilized with ZnOr$_2$ have better thermal stability by comparison than those containing commercial Ca/Zn stabilizers. However, the thermal stability time of PVC samples descended to 340 s after adding 3 phr Or. This result indicates that the Or structure containing carboxyl groups was not able to absorb the HCl liberated by PVC, and the existence of free acidic groups will promote the degradation of PVC. The thermal stability of the zinc salt stabilizer used in this paper, ZnOr$_2$, has a similar effect to the Ca/Zn commercial thermal stabilizer. Hence, it is clear that ZnOr$_2$ has a strong ability to absorb HCl, and can be applied as an potential thermal stabilizer [27,28].

![Figure 3. The effects of thermal stability time for poly(vinyl chloride) (PVC) with different kinds of thermal stabilizers at 180 °C.](image)
Figure 4 shows the effects of discoloration for PVC with different kinds of thermal stabilizers at 180 °C in air [27,28]. The PVC strip containing only 3 phr ZnSt$_2$ showed outstanding initial color, but turned absolutely black within 10 min. The reason is that ZnSt$_2$ can restrain discoloration by superseding the labile chlorine atoms on PVC chains and producing the undesirable ZnCl$_2$. Moreover, the PVC sample will suddenly turn black with the increase of ZnCl$_2$ content; this adverse effect on the long-term stability of PVC is called the “zinc burning” phenomenon. Furthermore, the complete discoloration time was delayed to 60 min for PVC samples stabilized with Ca/Zn (1:1) thermal stabilizer, which is mainly put down to the interaction between ZnCl$_2$ and CaSt$_2$. A remarkable improvement was observed in that ZnOr$_2$ could postpone the complete discoloration time, contrasted with ZnSt$_2$ and Ca/Zn (1:1) [29]. Meanwhile, as shown in Figures 3 and 4, a PVC strip stabilized with ZnOr$_2$ showed better initial colors than pure PVC, and the PVC strip stabilized with ZnSt$_2$. This demonstrates that ZnOr$_2$, just like ZnSt$_2$, can also supersede the labile chlorine atoms and prevent the formation of conjugated double bonds in PVC chains in the preliminary stage of degradation. The formation of these bonds can result in the discoloration of PVC [30].

![Figure 4](image_url)

Figure 4. The effects of discoloration for PVC with different kinds of thermal stabilizers at 180 °C.

The TGA curves of the pure PVC and PVC stabilized with 3% stabilizers are shown in Figure 5. From the figure, we can see that the thermal degradation process of PVC can be divided into two stages. The first stage involves the evolution of hydrogen chloride, which occurs principally in the range of 180–380 °C. The second stage involves chain breaking and crosslinking, and the release of hydrogen chloride, aromatic compounds, and polyenic compounds, which occurs primarily in the range of 380–550 °C. The effect of thermal stabilizers is chiefly reflected at the first stage [31,32]. Table 1 summarizes the relevant data about initial decomposition temperature ($T_{5\%}$ and $T_{10\%}$), most rapid decomposition temperature ($T_{r}$), and weight loss at the first stage ($W_f$) from the TGA curves. It can be observed that the pure PVC retained 29.6% of its weight at the first stage ($W_f$), and PVC stabilized by ZnOr$_2$ or CaSt$_2$/ZnOr$_2$ retained more weight (about 35.7% and 35.9%, respectively) than pure PVC. The greater residual weight was put down to ZnOr$_2$ absorbing the HCl liberated by the degradation of PVC [31,32]. Moreover, this phenomenon can also prevent the shortcoming of rapid degradation of PVC, because ZnOr$_2$ can effectively absorb HCl, reduce its concentration, and then delay the rapid degradation of PVC. This result can explain why PVC with ZnOr$_2$ has higher thermal stability.

| Stabilizer | Degradation time,*10min |
|------------|-------------------------|
| Pure PVC   |                         |
| ZnOr$_2$   |                         |
| Ca/Zn      |                         |
| Or         |                         |
| ZnSt$_2$   |                         |
Figure 5. The TGA curves of PVC stabilized with various thermal stabilizers.

Table 1. The TGA results of pure PVC and PVC stabilized with various thermal stabilizers.

| PVC/Stabilizer | T_{5\%} | T_{10\%} | T_r | W_f (%) |
|----------------|---------|----------|-----|---------|
| PVC           | 242.7   | 257.0    | 287.6 | 29.6    |
| PVC/ZnOr_{2}  | 224.6   | 238.5    | 273.6 | 35.7    |
| PVC/ZnOr_{2}/CaSt_{2} | 238.5 | 249.5    | 288.5 | 35.9    |

For the sake of suggesting a conceivable mechanism which could clarify the stabilizing efficiency of ZnOr_{2}, two experiments were executed to research the mode of behavior of ZnOr_{2} as a thermal stabilizer for PVC [33]. According to the first experiment, white sediment was observed in the pellucid filtrate when one drop of 0.1 mol/L silver nitrate solution was added in. This indicated the existence of chloride ions in the filtrate, and ultimately demonstrated that ZnOr_{2} could carry out a reaction with HCl at 180 °C. Moreover, Figure 6 gives the FTIR spectrum of ZnOr_{2} before and after treatment with HCl at 180 °C. The bands of the HCl-treated sample at 1523.8, 1329.5, and 983.9 cm^{-1} were put down to the asymmetric deformation vibrations, symmetric deformation vibrations, and rocking vibrations of NH_{2}^+, respectively. It can also be seen that the FTIR spectrum of the treated sample shows a band at 732.1 cm^{-1} specific for C–Cl, which confirms that ZnOr_{2} plays the part of an HCl absorber [34].

Figure 6. The FTIR spectra of ZnOr_{2} before (a) and after (b) treatment by HCl at 180 °C for 1 h in the ranges of 4000–500 cm^{-1} (left) and 1700–500 cm^{-1} (right).

Another experiment was executed to research whether ZnOr_{2} could supersede the labile chlorine atoms on a PVC chain [30,34]. A certain amount of ZnOr_{2} and PVC powder was mingled on a two-wheel open mill for 10 min at 180 °C. After dissolution of the PVC stabilized with ZnOr_{2} into...
tetrahydrofuran and subsequent filtering separation, the unreacted ZnOr\textsubscript{2} was eliminated. Finally, the PVC sample was precipitated through methanol and gathered by filtration.

The FTIR spectra of ZnOr\textsubscript{2}, the purified PVC/ZnOr\textsubscript{2} sample after ageing for 0 min, and pure PVC are shown in Figure 7a,c,d, respectively. It can be seen that the FTIR spectrum of the purified PVC/ZnOr\textsubscript{2} sample after ageing for 0 min indicated the existence of a new peak at 1677.7 cm\(^{-1}\) corresponding to the (-\text{\textasciitilde\text{\textasciitilde}CO\text{\textasciitilde\textasciitilde}}\text{-}) group in ZnOr\textsubscript{2}. This feature indicates that chemical bonds form between the orotate anion in ZnOr\textsubscript{2} and the degraded polymeric chains during the stabilization process. Moreover, the FTIR spectrum of the purified PVC/ZnOr\textsubscript{2} sample after ageing for 40 min is shown in Figure 7b. It can be seen that this fresh peak becomes weak and cannot be observed after being aged for 40 min \cite{28}. These results suggest that the (-\text{\textasciitilde\text{\textasciitilde}CO\text{\textasciitilde\textasciitilde}}\text{-}) group in ZnOr\textsubscript{2} may play a major role in suppressing the thermal degradation of PVC.

![Figure 7](image-url)

**Figure 7.** The FTIR spectra of PVC degradation process. (a) ZnOr\textsubscript{2}, (b) PVC/ZnOr\textsubscript{2}—40 min, (c) PVC/ZnOr\textsubscript{2}—0 min, (d) PVC.

According to the above-mentioned experimental results, a conceivable mechanism for PVC stabilized by ZnOr\textsubscript{2} is suggested in Scheme 2. On the basis of the mechanism diagram, the unstable chlorine atom (allyl chloride) on the PVC chain is first separated as a chloride ion and then left behind a carbocation on the polymer chain (1). The separated chlorine ion is absorbed by ZnOr\textsubscript{2}, leading to formation of orotate anion intermediates and ZnCl\textsubscript{2} (2 and 3). The orotate anion intermediates are appended to the positive charge generated on the PVC chain (4). This suggests that ZnOr\textsubscript{2} can postpone further zipper degradation by superseding the labile chlorine atoms in PVC chains. In addition, the orotate anions in ZnOr\textsubscript{2} have intense ability to absorb the hydrogen chloride liberated by the degradation of PVC (5 and 6), which will reduce the formation of ZnCl\textsubscript{2}. It has been declared that “zinc burning” occurs only after ZnCl\textsubscript{2} concentrations reach a certain level. As a result, ZnOr\textsubscript{2} provides higher long-term stabilizing efficiency than ZnSt\textsubscript{2} and Ca/Zn thermal stabilizers.
Scheme 2. The mechanism process of ZnOr₂ applied to stabilize PVC.
3.3. Influence of Mixed Thermal Stabilizers on Thermal Stability of PVC

From the aforementioned study result, it can be observed that ZnOr$_2$ has a better ability to replace unstable chlorine atoms and assimilate HCl than some commercial eco-friendly thermal stabilizers (ZnSt$_2$, etc.), and so it can availably improve the thermal stability of PVC by itself. However, ZnOr$_2$ cannot provide superior thermal stability compared with traditional lead salt stabilizers. Hence, in order to create more high-efficiency and eco-friendly thermal stabilizers, it should be integrated with other stabilizers (metal soap, auxiliary stabilizers, etc.) to manufacture complex thermal stabilizers [3,35]. This study includes an investigation of choosing calcium stearate (CaSt$_2$) as a traditional metal soap stabilizer, with DBM and PER as auxiliary thermal stabilizer.

The results of the Congo red test for PVC with various concentration ratios of CaSt$_2$/ZnOr$_2$ and CaSt$_2$/ZnSt$_2$ thermal stabilizers are shown in Figures 8 and 9, severally. It can be observed from Figure 8 that the thermal stability time of PVC/ZnOr$_2$ was correspondingly short, but could be increased by increasing the CaSt$_2$ concentration from 0.0 to 2.4. CaSt$_2$ can react with ZnCl$_2$ to produce CaCl$_2$, which can suppress the catalytic degradation of PVC, so that the thermal stability time of the PVC samples was step by step improved with increasing CaSt$_2$ content [3,35]. Interestingly, it was observed that the thermal stability time of PVC was decreased if only used with CaSt$_2$. The reason is that there are good synergy effect between ZnOr$_2$ and CaSt$_2$, which can efficaciously enhance the thermal stability of PVC. For another, Figure 9 also shows similar testing results: that the thermal stability time of PVC/ZnSt$_2$/CaSt$_2$ was increased with the increasing of CaSt$_2$ concentration [3,35]. By comparing Figures 8 and 9, it can be confirmed that ZnOr$_2$ displays a better stabilizing effect for PVC than the commercial thermal stabilizer ZnSt$_2$.

**Figure 8.** The effects of thermal stability time for PVC with different proportion of CaSt$_2$/ZnOr$_2$ thermal stabilizers at 180 °C.

**Figure 9.** The effects of thermal stability time for PVC with different proportion of CaSt$_2$/ZnSt$_2$ thermal stabilizers at 180 °C.
The results of the oven discoloration test for PVC with various concentration proportions of CaSt$_2$/ZnOr$_2$ and CaSt$_2$/ZnSt$_2$ thermal stabilizers are shown in Figures 10 and 11, severally [36]. From Figure 10, it can be observed that the PVC samples with various proportions of CaSt$_2$/ZnOr$_2$ thermal stabilizers showed consistent results with the Congo red test. The discoloration degree of PVC samples was also continuously delayed when the CaSt$_2$ content was increased gradually. This result also can be considered to mean CaSt$_2$ has an active effect for improving the long-term stability of PVC/ZnOr$_2$ [28,37]. Entertainingly, it can be observed that the effect of thermal stability was highest when the content proportion of the CaSt$_2$/ZnOr$_2$ was 1.8:1.2. Compared with other proportions, it was found that the complete black time of PVC reached 190 min, as well as its initial whiteness being prominently improved. It was also proven that a good synergy effect took place between ZnOr$_2$ and CaSt$_2$ and availably enhanced the thermal stability of PVC. By comparing Figures 10 and 11, it can be shown that the CaSt$_2$/ZnOr$_2$ complex stabilizer has a generally more stable effect than CaSt$_2$/ZnSt$_2$, which can ultimately indicate that ZnOr$_2$ has a better stabilizing effect than the ZnSt$_2$ thermal stabilizer.

![Figure 10](image1.png)

**Figure 10.** The effects of discoloration for PVC with different proportion of CaSt$_2$/ZnOr$_2$ thermal stabilizers at 180 °C.

![Figure 11](image2.png)

**Figure 11.** The effects of discoloration for PVC with different proportion of CaSt$_2$/ZnSt$_2$ thermal stabilizers at 180 °C.

It is well known that an auxiliary stabilizer should be added to Ca/Zn stabilizers to improve their thermal stability in practical application. Therefore, it was expected to produce a synergistic stabilization effect on PVC when CaSt$_2$/ZnOr$_2$ stabilizer was combined with the auxiliary stabilizers dibenzoylmethane (DBM) and pentaerythritol (PER), commonly used β-diketone and polyols, respectively. They are also the most frequently used organic auxiliary thermal stabilizers for PVC. To this end, these two commercial compounds were studied as auxiliary stabilizers for CaSt$_2$/ZnOr$_2$ stabilizers.
Figures 12 and 13 respectively show PVC Congo red and oven discoloration test results with various ratios of CaSt$_2$/ZnOr$_2$/DBM thermal stabilizers. As shown in Figure 12, it can be observed that the stability time of PVC/CaSt$_2$/ZnOr$_2$/DBM samples was longer than PVC/CaSt$_2$/ZnOr$_2$ samples. Hence, it was indicated that addition of DBM could availably contribute to enhancing the stability time of PVC [28,37]. Moreover, it can be seen from Figure 13 that the initial whiteness of PVC samples was decreased, as well as the long-term stability being greatly enhanced, when auxiliary stabilizer DBM was added. It is suggested that there are several groups on the structure of DBM which have the capacity to supersede unstable chlorine atom as well as ZnOr$_2$. A competition to replace unstable chlorine atoms on PVC occurred between DBM and ZnOr$_2$, which led to the decrease of the initial whiteness of PVC samples. Furthermore, the long-term stability of the PVC was greatly improved after the addition of DBM. Metal complexes formed between DBM and ZnCl$_2$, so that the ZnOr$_2$ had more effectively capacity to absorb HCl. The synergy effect between DBM and ZnOr$_2$ effectively improves the long-term stability of PVC. From the above mentioned, it can be confirmed that ZnOr$_2$ provided valid initial stability as well as inferior long-term stability. Moreover, the addition of DBM to PVC/ZnOr$_2$ is not necessary because DBM also plays an important role in inhibiting coloring ability of the PVC at early stages.

![Figure 12](image12.png)

**Figure 12.** The effects of thermal stability time for PVC with different proportions of CaSt$_2$/ZnOr$_2$/DBM thermal stabilizers at 180 °C.

![Table 1](image12.png)

**Table 1.** The effects of discoloration for PVC with different proportions of CaSt$_2$/ZnOr$_2$/DBM thermal stabilizers at 180 °C.

Figures 14 and 15 respectively show PVC Congo red and oven discoloration test results with various ratios of CaSt$_2$/ZnOr$_2$/PER thermal stabilizers. As shown in Figure 14, it was observed that the stability times of PVC/CaSt$_2$/ZnOr$_2$/PER samples were higher than PVC/CaSt$_2$/ZnOr$_2$ samples. Hence, it is indicated that addition of PER can availably contribute to enhancing the stability time of PVC [28,37]. Moreover, the result was different with addition of DBM. It can be seen from Figure 15...
that the initial whiteness of PVC samples maintained a relatively high level, while the long-term stability was markedly improved when auxiliary stabilizer PER was added. ZnO\textsubscript{2} possesses the ability to both replace unstable chlorine atoms and absorb HCl, while PER has the capacity to complex with ZnCl\textsubscript{2}. The synergistic effect between them effectively improved the initial stability and long-term stability of the PVC. Thus, it can be considered that PER is an appropriate auxiliary stabilizing agent for PVC/CaSt\textsubscript{2}/ZnO\textsubscript{2}.

![Figure 14. The effects of thermal stability time for PVC with different proportions of CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER thermal stabilizers at 180 °C.](image)

| CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER (phr/phr/phr) | Degradation time,*10min |
|---------------------------------------------------------------|-------------------------|
| 3.0/0.0/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |
| 2.4/0.6/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |
| 1.8/1.2/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |
| 1.2/1.8/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |
| 0.6/2.4/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |
| 0.0/3.0/0.9                                                   | 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 |

![Figure 15. The effects of discoloration for PVC with different proportions of CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER thermal stabilizers at 180 °C.](image)

In order to ultimately prove the experimental results of the Congo red and oven discoloration tests, the relationship between weight and time of PVC, PVC/ZnO\textsubscript{2}, PVC/CaSt\textsubscript{2}/ZnO\textsubscript{2}, PVC/CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER, and PVC/ZnSt\textsubscript{2} was characterized by thermogravimetric analysis at a specific temperature about 220 °C for 2 h, and the results are summarized in Figure 16 [27,35]. It can be observed from the figure that the sequence for loss of thermal weight is as follows: PVC/CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER > PVC/CaSt\textsubscript{2}/ZnO\textsubscript{2} > PVC/ZnO\textsubscript{2} > PVC/ZnSt\textsubscript{2}. It can therefore be confirmed that the thermal stability of ZnO\textsubscript{2} is better than ZnSt\textsubscript{2}. Moreover, the thermal stability was greatly increased after the addition of CaSt\textsubscript{2} and auxiliary stabilizer PER. The results of thermogravimetric analysis agreed with the Congo red and oven discoloration method. Therefore, it can be verified that both CaSt\textsubscript{2} and PER take a synergistic effect with ZnO\textsubscript{2} to improve the thermal stability of PVC. Hence, the complex of CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER can be considered a high-efficiency thermal stabilizer.
Figure 16. The TGA curves of pure PVC and PVC stabilized with various complex thermal stabilizers with keeping 220 °C for 2 h.

4. Conclusions

ZnO\textsubscript{2} was successfully synthesized by a straightforward precipitation method, and characterized through elemental analysis, FTIR spectroscopy, and TGA. ZnO\textsubscript{2} was demonstrated to be an valid thermal stabilizer for PVC. Contrasted with ZnSt\textsubscript{2}, ZnO\textsubscript{2} can effectively postpone the “zinc burning” of PVC. After combining with CaSt\textsubscript{2}, the CaSt\textsubscript{2}/ZnO\textsubscript{2} complex can also improve the long-term stability of PVC remarkably. In order to improve the thermal stability of PVC, DBM and PER were added as auxiliary stabilizers into CaSt\textsubscript{2}/ZnO\textsubscript{2}, to prepare complex thermal stabilizers. Both of the two auxiliary stabilizers displayed good long-term stability for PVC when combined with CaSt\textsubscript{2}/ZnO\textsubscript{2}. Moreover, PER has a valid synergistic effect with CaSt\textsubscript{2}/ZnO\textsubscript{2} that enhances the initial whiteness of PVC. Therefore, CaSt\textsubscript{2}/ZnO\textsubscript{2}/PER can be applied as a potential high efficiency complex thermal stabilizer for PVC in the future.

Author Contributions: F.Y., H.H.Z. and X.W. conceived and designed the experiments. Y.Q.G., X.T.M., and Y.Y.X. performed the experiments and analyzed the data. F.Y. and Q.F.Y. wrote the paper. F.Y. and Q.F.Y. provided the funds and revised the paper. All authors discussed the results and improved the final text of the paper.

Funding: The authors are grateful for the financial support from the [National Natural Science Foundation of China] grant number [51703129], [Shaoxing Science and Technology Project] grant number [2017B70045] and [The Undergraduate Scientific and Technological Innovation Project] grant number [2018R432026]. The APC was funded by [51703129] and [2017B70045].

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Avalos, A.S.; Hakkarainen, M.; Odellius, K. Superiorly plasticized PVC/PBSA blends through crotonic and acrylic acid functionalization of PVC. Polymers 2017, 9, 84. [CrossRef]
2. Sabaa, M.W.; Rabie, S.T.; Mohamed, R.R. Novel antimicrobial and antitumor organic thermal stabilizers for rigid Poly (vinyl chloride). J. Therm. Anal. Calorim. 2012, 109, 1503–1513. [CrossRef]
3. Shnawa, H.A.; Jahani, Y.; Khalaf, M.N.; Taobi, A.H. The potential of tannins as thermal co-stabilizer additive for polyvinyl chloride. J. Therm. Anal. Calorim. 2016, 123, 1253–1261. [CrossRef]
4. Shnawa, H.A. Thermal stabilization of polyvinyl chloride with traditional and naturally derived antioxidant and thermal stabilizer synthesized from tannins. J. Therm. Anal. Calorim. 2017, 129, 789–799. [CrossRef]
5. Wu, B.Z.; Wang, Y.T.; Chen, S.; Wang, M.Y.; Ma, M.; Shi, Y.Q.; Wang, X. Bis-uracil based high efficient heat stabilizers used in super transparent soft poly (vinyl chloride). Polym. Degrad. Stab. 2018, 149, 143–151. [CrossRef]
6. Xie, L.H.; Li, D.G.; Fu, M.; Zhang, J.; Zhang, L.P.; Zhang, Y.L.; Zhao, P. Study on lanthanum-pentaerythritol alkoxide as a thermal stabilizer for rigid polyvinyl chloride. J. Vinyl Addit. Technol. 2017, 23, 55–61. [CrossRef]
7. Wang, M.; Li, H.X.; Huang, X.L.; Yi, L. Zinc Maleate and Calcium Stearate as a Complex Thermal Stabilizer for Poly(vinyl chloride). *J. Vinyl Addit. Technol.* **2014**, *20*, 1–9. [CrossRef]

8. Sabaa, M.W.; Farag, Z.R.; Mohamed, N.A. Thermal Degradation Behavior of poly(vinyl chloride) in the Presence of poly(glycidyl methacrylate). *J. Appl. Polym. Sci.* **2008**, *110*, 2205–2210. [CrossRef]

9. Zeddam, C.; Belhaneche-Bensemra, N. Application of FT-IR spectroscopy to the specific migration study of an organotin heat stabilizer from rigid poly(vinyl chloride) into food simulants. *Polimery* **2011**, *56*, 657–661. [CrossRef]

10. Liu, J.P.; Shang, H.Z.; Zheng, Y.B.; Song, X. Synthesis and evaluation of poly (dioctyltin maleate-styrene-methyl acrylate) as a stabilizer for poly(vinyl chloride). *J. Appl. Polym. Sci.* **2009**, *113*, 1216–1222. [CrossRef]

11. Bjorn, A.; Horsing, M.; Karlsson, A.; Mersiowsky, I.; Ejlertsson, J. Impacts of temperature on the leaching of organotin compounds from poly(vinyl chloride) plastics—A study conducted under simulated landfill conditions. *J. Vinyl Addit. Technol.* **2007**, *13*, 176–188. [CrossRef]

12. Wang, M.; Song, X.H.; Jiang, J.C.; Xia, J.L.; Li, M. Binary amide-containing tung-oil-based Ca/Zn stabilizers: Effects on thermal stability and plasticization performance of poly(vinyl chloride) and mechanism of thermal stabilization. *Polym. Degrad. Stab.* **2017**, *143*, 106–117. [CrossRef]

13. Fang, L.; Song, Y.H.; Zhu, X.N.; Chen, S.H.; Du, P.H.; Zheng, Q.A. Influence of lanthanum stearate and calcium/zinc stabilizers on stabilization efficiency of dibutyltin dilaurate to polyvinyl chloride. *Chin. J. Polym. Sci.* **2010**, *28*, 637–645. [CrossRef]

14. Wang, M.; Xia, J.L.; Jiang, J.C.; Li, S.H.; Huang, K.; Mao, W.; Li, M. A novel liquid Ca/Zn thermal stabilizer synthesized from tung-maleic anhydride and its effects on thermal stability and mechanical properties of PVC. *Polym. Degrad. Stab.* **2016**, *133*, 136–143. [CrossRef]

15. Huanzhang, C.H.E.N.; Hua, L.I.; Hong, L.I. Study on preparation and performance of zinc cyanurate thermal stabilizer for PVC. *J. Hebei Univ. Sci. Technol.* **2016**, *37*, 33–38.

16. Xu, X.P.; Chen, S.; Tang, W.; Qu, Y.J.; Wang, X. Investigation of basic zinc cyanurate as a novel thermal stabilizer for poly(vinyl chloride) and its synergistic effect with calcium stearate. *Polym. Degrad. Stab.* **2014**, *99*, 211–218. [CrossRef]

17. Zhu, L.Z.; Wu, Y.J.; Shentu, B.Q.; Weng, Z.X. Preparation and characterization of zinc-mannitol complexes as PVC thermal stabilizers with high efficiency. *Polym. Degrad. Stab.* **2016**, *133*, 399–403. [CrossRef]

18. Li, S.M.; Yao, Y.W. Effect of thermal stabilizers composed of zinc barbiturate and calcium stearate for rigid poly(vinyl chloride). *Polym. Degrad. Stab.* **2011**, *96*, 637–641. [CrossRef]

19. Starnes, W.H., Jr.; Jennings, T.C.; Krauskopf, L.G. *Plastics Additives Handbook*, 6th ed.; Hanser Publishers: Munich, Germany, 2005; Chapter 3.

20. Santamaria, E.; Edge, M.; Allen, N.S.; Harvey, H.B.; Mellor, M.; Orchison, J. New Insights into the Degradation Mechanism of Poly (Vinyl Chloride), Part (III): Implementation of New Costabilizers—Towards Heavy Metal Free Systems (HMFS). *J. Appl. Polym. Sci.* **2005**, *96*, 122–143. [CrossRef]

21. Chen, S.; Xu, X.P.; Zhang, J.H.; Tang, W.; Qu, Y.J.; Wang, X. Efficiency and mechanism for the stabilizing action of N,N′-bis(phenylcarbamoyl)alkyldiamines as thermal stabilizers and co-stabilizers for poly(vinyl chloride). *Polym. Degrad. Stab.* **2014**, *105*, 178–184. [CrossRef]

22. Li, M.; Zhang, J.W.; Xin, J.N.; Huang, K.; Li, S.H.; Wang, M.; Xia, J.L. Design of green zinc-based thermal stabilizers derived from tung oil fatty acid and study of thermal stabilization for PVC. *J. Appl. Polym. Sci.* **2017**, *134*, 44679. [CrossRef]

23. Li, M.; Jiang, J.C.; Zhang, J.W.; Yang, X.H.; Zhang, Y.; Li, S.H.; Song, J.; Huang, K.; Xia, J.L. Preparation of a new liquid thermal stabilizer from rosin and fatty acid and study of the properties of the stabilized PVC. *Polym. Degrad. Stab.* **2014**, *109*, 129–136. [CrossRef]

24. Li, M.; Liang, Y.D.; Wu, Y.X.; Li, K.S. Synergistic effect of complexes of ethylenediamine double maleamic acid radical and lanthanum(III) with pentaerythritol on the thermal stability of poly(vinyl chloride). *Polym. Degrad. Stab.* **2017**, *140*, 176–193. [CrossRef]

25. Li, M.; Zhang, J.W.; Huang, K.; Li, S.H.; Jiang, J.C.; Xia, J.L. Mixed calcium and zinc salts of dicarboxylic acids derived from rosin and dipentene: Preparation and thermal stabilization for PVC. *RSC Adv.* **2014**, *4*, 63576–63585. [CrossRef]

26. Wang, M.; Song, X.H.; Jiang, J.C.; Xia, J.L.; Li, M. Influence of Zeolitic imidazolate framework-8 on the thermal stabilization of poly(vinyl chloride). *Polym. Degrad. Stab.* **2018**, *149*, 112–118. [CrossRef]
27. Wu, B.Z.; Wang, Y.T.; Chen, S.; Wang, M.Y.; Ma, M.; Shi, Y.Q.; Wang, X. Stability, mechanism and unique “zinc burning” inhibition synergistic effect of zinc dehydroacetate as thermal stabilizer for poly(vinyl chloride). *Polym. Degrad. Stab.* 2018, 152, 228–234. [CrossRef]

28. Shi, Y.Q.; Chen, S.; Ma, M.; Wu, B.Z.; Ying, J.; Xu, X.P.; Wang, X. Highly efficient and antibacterial zinc norfloxacin thermal stabilizer for poly(vinyl chloride). *RSC Adv.* 2016, 6, 97491–97502. [CrossRef]

29. Wang, M.; Song, X.H.; Jiang, J.C.; Xia, L.; Li, S.H.; Li, M. Excellent hydroxyl and nitrogen rich groups-containing tung-oil-based Ca/Zn and polyol stabilizers for enhanced thermal stability of PVC. *Thermochim. Acta* 2017, 658, 84–92. [CrossRef]

30. Zhang, D.F.; Yao, S.; Li, S.; Wang, J.; Yao, Y.W. A novel La-containing additive for the long-term thermal stabilization of poly(vinyl chloride). *Polym. Degrad. Stab.* 2017, 144, 187–194. [CrossRef]

31. Khaleghi, M.; Didehban, K.; Shabanian, M. Effect of new melamine-terephthaldehyde resin modified graphene oxide on thermal and mechanical properties of PVC. *Polym. Test.* 2017, 63, 382–391. [CrossRef]

32. Zhang, Z.; Wang, S.C.; Zhang, J.; Zhu, W.Q.; Tian, T.S. Remarkably improved toughness and thermal stability of poly (vinyl chloride) (PVC)/poly (alpha-methyl-styrene-acrylonitrile) (alpha-MSAN) blend with the assistance of two impact modifiers. *Polym. Test.* 2016, 51, 1–5. [CrossRef]

33. Mohamed, N.A. Biologically active maleimido aromatic 1,3,4-oxadiazole derivatives evaluated thermogravimetrically as stabilizers for rigid PVC. *J. Therm. Anal. Calorim.* 2018, 131, 2535–2546. [CrossRef]

34. Jiang, P.P.; Song, Y.Y.; Dong, Y.M.; Yan, C.R.; Liu, P. Zinc glycerolate with lanthanum stearate to inhibit the thermal degradation of poly(vinyl chloride). *J. Appl. Polym. Sci.* 2013, 127, 3681–3686. [CrossRef]

35. Du, Y.G.; Gao, J.G.; Liu, X.Q.; Yang, J.B. Influence of Nano-CeO₂ as Co-Stabilizer on the Thermal Stabilization Efficiency of Novel Calcium/Zinc Soap Stabilizers for Poly(vinyl chloride). *J. Vinyl Addit. Technol.* 2014, 20, 243–249. [CrossRef]

36. Ye, F.; Guo, X.J.; Zhan, H.H.; Lin, J.X.; Lou, W.C.; Ma, X.T.; Wang, X. The synergistic effect of zinc urate with calcium stearate and commercial assistant stabilizers for stabilizing poly(vinyl chloride). *Polym. Degrad. Stab.* 2018, 156, 193–201. [CrossRef]

37. Li, M.; Duan, C.; Wang, H.O.; Liu, Z.G.; Wang, M.T.; Hu, Y.H. Lanthanum histidine with pentaerythritol and zinc stearate as thermal stabilizers for poly(vinyl chloride). *J. Appl. Polym. Sci.* 2016, 133, 42878. [CrossRef]