

# Study on Pentaerythritol–Zinc as a Novel Thermal Stabilizer for Rigid Poly(Vinyl Chloride)

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**ABSTRACT:** Pentaerythritol–zinc (penzinc) was prepared by a solid-phase reaction technique. The principal volatile products of the reaction between pentaerythritol and ZnO were analyzed with a coupled thermogravimetry–mass spectrometry system. The results indicated that a large amount of water was formed at the reaction temperature. Scanning electron microscopy (SEM) results showed the appearance of penzinc as flaky particles. Accordingly, the penzinc obtained through the dehydration between pentaerythritol and ZnO is likely to be a monopentaerythritol complex, such as zinc monoglycerolate. The thermal stability of poly(vinyl chloride) (PVC) with penzinc as a thermal stabilizer was investigated by a Congo Red test, Oven aging test and thermal gravimetric

analysis (TGA). The Congo Red test showed the thermal stability time of PVC with penzinc was 38 min, longer than those with commercial thermal stabilizers. TGA indicated that the penzinc had little impact on the thermal degradation of PVC, but could increase the mass of residues. Oven aging test showed that the penzinc could significantly retard the discoloration during the long-term decomposition of PVC. Meanwhile, no “zinc burning” was observed in the PVC with penzinc. These results indicate that the penzinc is an excellent thermal stabilizer for rigid PVC. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** pentaerythritol–zinc; rigid PVC; thermal stabilizer; Congo Red test; Oven aging test

## INTRODUCTION

It is generally known that poly(vinyl chloride) (PVC) is quite unstable when exposed to high temperatures, oxygen, light, and mechanical energy during its processing and applications.<sup>1</sup> Despite the instability of this polymer, its easy modification, low cost, and excellent chemical and physical properties have made PVC widely used in industry. During the thermal degradation, PVC undergoes autocatalytic dehydrochlorination followed by the formation of conjugated polyene sequences.<sup>2–4</sup> Finally, the degradation results in undesirable discoloration of PVC, meanwhile the physical and chemical properties of the polymer change drastically.<sup>5</sup> It is generally believed that this instability is obtained from various defect sites in PVC such as allyl chloride, tertiary hydrogen, chlorine atoms associated with branches, and head-to-head structures.<sup>1,6,7</sup> To solve this problem, various methods have been developed.<sup>8–10</sup> Among these methods, adding thermal stabilizers into PVC to resist thermal degradation is the most efficient

and practical way. Generally, the thermal stabilizers have two main functions: (i) it can react with the labile chlorine atoms in PVC chains to retard further dehydrochlorination<sup>4</sup>; (ii) it can react with HCl released in the degradation process of PVC, thus retarding its catalytic effects.<sup>11</sup> Lead salts,<sup>12</sup> organic tin,<sup>13,14</sup> metal soaps,<sup>15–18</sup> organic compounds,<sup>19–21</sup> and rare earth elements<sup>22</sup> have been investigated as thermal stabilizers in PVC. Despite the high efficiency of lead-based materials and organic tin, their wide applications are restricted owing to their toxicity. Recently, metal soaps are attracting more and more attention as thermal stabilizers because they are nontoxic; however, the low antidegradation efficiency of these materials has become the technical bottleneck. The most studied and used metal soap is Ca/Zn thermal stabilizer. However, the strong Lewis acid ZnCl<sub>2</sub> formed from Ca/Zn thermal stabilizer in PVC may catalyze the decomposition of this polymer resulting in sudden black coloration followed by a drastic decline of mechanical properties.<sup>23,24</sup> Therefore, it is of interest to find a new type of zinc-based material which not only exhibits excellent thermal stability against degradation of PVC but has also no positive catalytic effects on the degradation of this polymer. Recently, pentaerythritol has been widely investigated as an important costabilizer, especially with zinc-based compounds, owing to its excellent thermal stabilization.<sup>25</sup> Dever and Guerini<sup>26,27</sup> have

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reported the synthesis of the pentaerythritol–zinc, and studied its dynamic thermal stability. The results show that in conjunction with other additives, the pentaerythritol–zinc can improve the thermal stability of PVC obviously.

In this article, the synthesis mechanism of pentaerythritol–zinc (penzinc) was studied. Furthermore, we mainly studied the thermal stability of the penzinc as a thermal stabilizer for rigid PVC. Experimental results demonstrated that PVC with penzinc has an excellent long-term thermal stability (The Discoloration time of PVC at 180°C can be extended to about 90 min). Meanwhile, the catalytic effect of the zinc-based thermal stabilizers on the decomposition of PVC has not been observed when the penzinc was used.

## EXPERIMENTAL

### Materials

PVC resin (average degree of polymerization: 1005, China Petrochemical Qilu); ZnO, pentaerythritol, and other chemical agents used were all of AR grade. Thermal stabilizers, for example Ca/Zn stabilizers, lead salt and low-lead salt stabilizers, were kindly supplied by Huike Additives, China. Ca/Zn stabilizer consisted of Calcium stearate (20 wt %), zinc stearate (30 wt %),  $\beta$ -diketone, phosphite ester, and other additives. The lead salt stabilizer is composed of tribasic lead sulfate, dibasic lead phosphite, and other additives. The content of PbO is about 40 wt %. As for the low-lead salt stabilizer, the content of PbO is 20 wt %.

### Preparation of penzinc

Pentaerythritol and ZnO in a molar ratio of 1.4 : 1 were put into a home mixer at 3000 r/min for 5 min. Penzinc was obtained after the homogeneous powder was put into an oven with a motor stirring at 120 r/min to react at 200–210°C for 2 h.

### Preparation of PVC samples

The PVC samples were prepared by mixing PVC (powder, 100 phr), stearic acid (powder, 1 phr), and the stabilizers (mixture, 4 phr) in a mixer. Then 56-g mixture was milled by an open twin-roller at 180°C for 5 min. The thickness of the drawn-out sheets was  $1.0 \pm 0.1$  mm.

### Test methods

The thermogravimetry (TG)–mass spectrometry (MS) experiments were performed with the TG-MS system (STA449C-QMS403C, Netzsch, Germany). The

operating conditions were as follows: purge gas, nitrogen of 99.9995% purity; MS range, 1–300 amu; heating rate, 10°C/min from 30 to 900°C in N<sub>2</sub>.

The morphology of the penzinc was determined using SEM Sirion 200, Netherlands. The samples were coated with gold using sputtering technique prior to observation.

Thermogravimetric and differential thermogravimetric analyses were evaluated for different PVC samples. The investigations were carried out under nitrogen atmosphere with flow rate 30 mL/min. Approximately, 20 mg sample was heated from room temperature to 700°C at a heating rate of 10°C/min.

### Thermal stability of penzinc

#### Congo Red test method

According to ASTM D4202, the PVC samples were cut into small squares of 0.2 mm  $\times$  0.2mm with a total weight of 2 g, and later they were put into a tube with Congo Red paper located at about 1.5 cm above the sample. The static thermal stability of samples was evaluated with the tube heated in oil bath at 180°C. The time was defined as Ts when Congo Red paper began to turn to blue.

#### Oven aging test

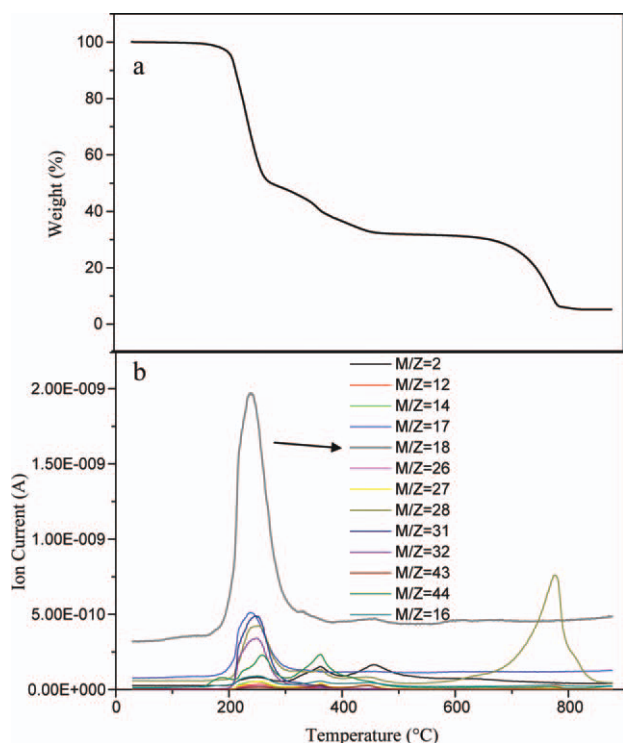
The PVC sheet was cut into small strips (10 mm  $\times$  10 mm). These strips were heated in a thermal aging test box at 180°C in air and subjected to static thermal aging. The samples were observed visually every 10 min.

## RESULTS AND DISCUSSION

### The synthesis mechanism and structure of penzinc

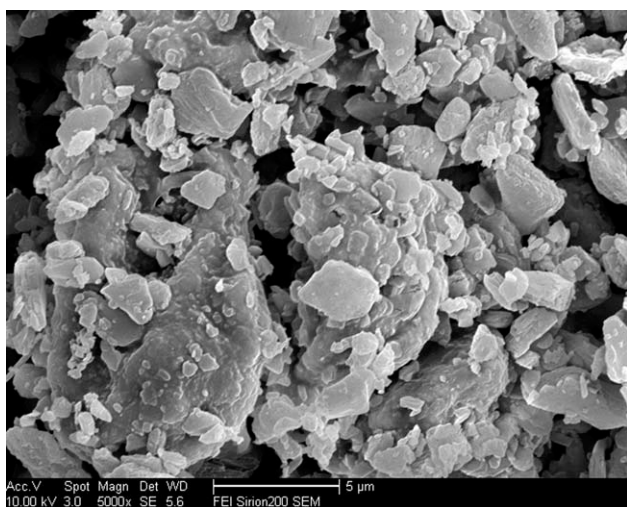
Figure 1 shows the TG–MS curves of the mixture (ZnO and pentaerythritol at the ratio of 1.4 : 1) heated at 10°C/min in nitrogen atmosphere. When the temperature was raised above 200°C, apparent weight loss occurred. From the MS curves, it can be seen that the major ionic fragment is H<sub>2</sub>O whose  $m/z$  value is 18. The result indicates that the reaction of pentaerythritol and ZnO generated a large amount of water. Figure 1(b) also shows that many adverse reactions took place when the temperature exceeds 210°C. Therefore, the ideal reaction temperature is between 200 and 210°C.

In general, alcohols are weak acid. The acidity of polyhydric alcohols is higher than that of the normal alcohol. For example, the  $pK_a$  of glycerol is 14.1. Therefore, pentaerythritol can react with ZnO to produce penzinc and H<sub>2</sub>O, just as the reaction of glycerol and ZnO to form CH<sub>2</sub>–O–Zn type bonds, during which water is generated.<sup>28</sup>

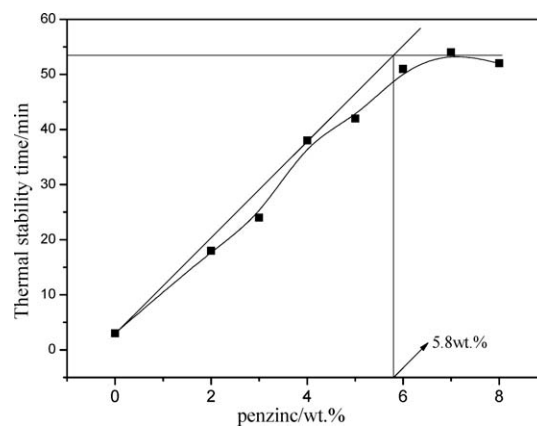


**Figure 1** TG-MS curves of the mixture (ZnO and pentaerythritol at the ratio of 1 : 1.4) heating at 10°C/min in nitrogen atmosphere. (a) TG curves; (b) MS curves. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

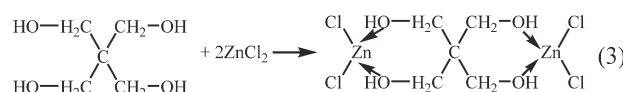
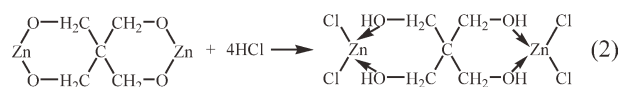
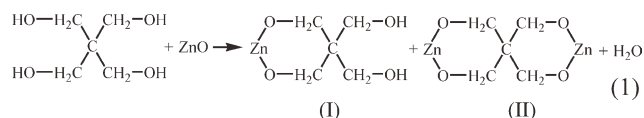
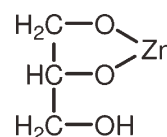
SEM image of the penzinc shown in Figure 2 was used to determine the size of the powder. As shown in Figure 2, it can be seen that most of the penzinc powders are two-dimensional flaky particles, just like the appearance of zinc monoglycerolate.<sup>29,30</sup> This result indicates that the structure of penzinc is like that of zinc monoglycerolate which is represented as below:



**Figure 2** Morphology of penzinc by scanning electron microscopy.



**Figure 3** Thermal stability time as a function of ratios of penzinc.

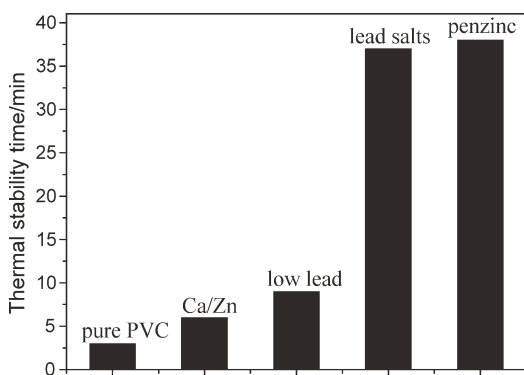


Therefore, the penzinc obtained through dehydration between pentaerythritol and ZnO is likely a mono-pentaerythritol complex, just as the zinc monoglycerolate. Moreover, as the penzinc is prepared by solid-phase reaction technique, the reaction cannot reach the end. The final product may be composed of structure (I and II) in Reaction (1) as well as unreacted pentaerythritol and ZnO. In this article, structure (II) is used to represent penzinc.

### Thermal stability of penzinc

Figures 3 and 4 show the influence of different amounts of penzinc and different additives on the thermal stability against degradation and dehydrochlorination process of PVC resins evaluated by Congo Red test. The result indicates that the penzinc greatly extends the thermal stability time ( $T_s$ ) of PVC as shown in Figure 3. It can be seen from the





**Figure 4** Comparison of  $T_s$  (thermal stability time) in PVC with different thermal stabilizers at the ratio of 4 wt %.

curve that the thermal stability time increases with increasing amounts of penzinc. The longest time is 54 min when the penzinc amount is 7 wt %. But the thermal stability time decreased as the amount of penzinc exceeded 7 wt %. To determine the optimal amount of penzinc as a single thermal stabilizer in PVC, the starting effect amount (short for SEA) has been defined. It was obtained graphically from the intersection of the extrapolations that the SEA value was 5.8 wt % (Fig. 3).

All the thermal stabilizers enhanced the  $T_s$  compared with pure PVC as shown in Figure 4. The  $T_s$  of pure PVC is only 3 min, whereas  $T_s$  of the lead salts is 37 min which has higher efficiency in retarding the release of HCl from PVC at 180°C. The  $T_s$  of Ca/Zn and the low-lead stabilizers are 6 and 9 min, respectively, illustrating their relatively low-thermal stability against degradation of PVC. Compared with all these commercially used thermal stabilizers,

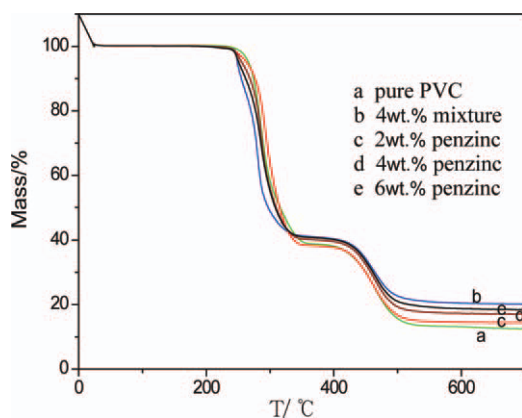
the penzinc has shown great improvement in  $T_s$  which is 38 min, 12 times greater than pure PVC and 6 times greater than Ca/Zn stabilizer. Meanwhile, one can see that the  $T_s$  of lead salts and penzinc are almost the same, suggesting that the efficiency of penzinc in stabilization of PVC is similar to that of lead salts which are considered as the most effective thermal stabilizers. The result may be explained as the excellent effect of penzinc in absorbing HCl gas released in the degradation process of PVC, as illustrated in Reaction (2). When PVC resin is exposed in air at the temperature of 180°C, HCl forms at different unstable sites in polymer matrix. Owing to the catalytic effect of HCl, PVC with no thermal stabilizers drastically decomposes when heated as shown in Figure 4, with the stability time of pure PVC being only 3 min.<sup>31</sup> It is generally accepted that one of the main effects of thermal stabilizer is to absorb HCl. As for penzinc, it shows great improvement in this aspect, which may be attributed to the high reactivity of penzinc with HCl released from PVC as is shown in Reaction (2).

#### Discoloration

Oven aging test was employed to determine the discoloration of PVC with different thermal stabilizers when exposed to air at 180°C. The result is summarized in Table I. Comparing all four samples, it is important to notice that PVC with thermal stabilizers showed no discoloration in the initial 10 min, suggesting that these compounds exhibit high efficiency in stabilization of PVC. As for Ca/Zn thermal stabilizers, with the time extended to 12 min, the mixture

**TABLE I**  
Discoloration of PVC Blends Exposed in Oven at 180°C in Air, the Ratio of Thermal Stabilizer was all 4 wt %

| Category  | Degradation time /min |    |    |    |    |    |     |     |     |     |
|-----------|-----------------------|----|----|----|----|----|-----|-----|-----|-----|
|           | 0                     | 10 | 30 | 50 | 70 | 90 | 110 | 130 | 150 | 170 |
| Lead salt |                       |    |    |    |    |    |     |     |     |     |
| Low lead  |                       |    |    |    |    |    |     |     |     |     |
| Ca/Zn     |                       |    |    |    |    |    |     |     |     |     |
| Penzinc   |                       |    |    |    |    |    |     |     |     |     |



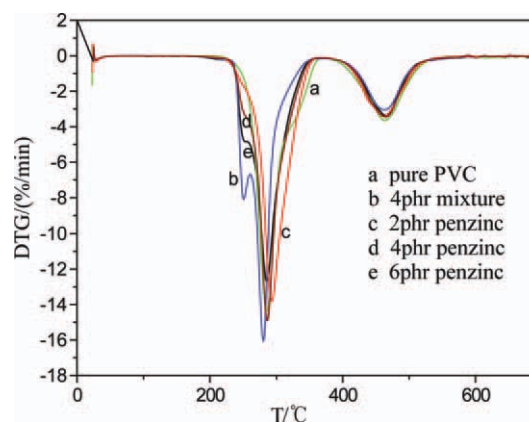
**Figure 5** TG curves for PVC with different ratios of penzinc or mixture at the heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

started turning black, which is attributed to the  $\text{ZnCl}_2$  formed between zinc stearate and HCl released from PVC when heated. It is widely known that  $\text{ZnCl}_2$  is a strong Lewis acid in catalyzing decomposition of PVC.<sup>21</sup> Although there is zinc in penzinc, it is important to notice that the PVC with penzinc showed no “sudden black” phenomenon, as summarized in Table I. The reason is that there is no free  $\text{ZnCl}_2$  formed in the degradation of the mixture, as illustrated in Reaction (2), thus no catalytic effect of  $\text{ZnCl}_2$  was observed. For long-term discoloration, the degradation of the polymer was much slower than pure PVC owing to the high efficiency of penzinc in absorbing HCl which acts as another catalytic agent in the decomposition of PVC. Thus discoloration of the mixture was much slower in the presence of penzinc. Meanwhile, as summarized in Table I the long-term discoloration of PVC with penzinc was slightly better than with the low-lead thermal stabilizer which is widely used in PVC pipe industry, but worse than PVC with the lead salt stabilizer.

### TG analysis

Figure 5 shows the TG analysis of PVC containing different amounts of thermal stabilizers conducted from room temperature to 700°C at a heating rate of 10°C/min in nitrogen. As shown in all five curves, there are two major weight loss stages: at the first stage, dehydrochlorination occurred and conjugated polyene sequences were formed; the second stage can be attributed to the thermal cracking of the carbonaceous conjugated polyenes sequences followed by the formation of aromatic hydrocarbon such as benzene and toluene.

To evaluate the thermal stability of the blends, the following characteristic parameters of two degradation steps were determined from the TG and DTG



**Figure 6** DTG curves for PVC with different ratios of penzinc or mixture (ZnO and pentaerythritol) at the heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

(Fig. 6) curves: the onset temperature  $T_s$ , the mass of residual at 700°C  $M_r$ , and the temperature at the maximum rate of PVC degradation in the first and the second degradation steps  $T_{\max 1}$ ,  $T_{\max 2}$ . The characteristic parameters obtained are listed in Table II.

As summarized in Table II, the  $T_s$  values of PVC in the presence of different ratios of penzinc are 275.8, 270.3, and 264.3 min, close to the  $T_s$  value of pure PVC, implying penzinc dose not affect the decomposition of PVC greatly. This may be explained as penzinc can absorb HCl easily released from PVC, but does not coordinate with the polymer matrix, thus exerts little effect on the formed conjugated polyene sequence. Similar values can be found in  $T_{\max 1}$  and  $T_{\max 2}$ . As for PVC in the mixture of ZnO and pentaerythritol in molar ratio of 1 : 1.4, the relatively short  $T_s$  compared with that of pure PVC could be attributed to the  $\text{ZnCl}_2$  (formed by ZnO and HCl released by PVC at 180°C) which is a strong Lewis acid in catalyzing the decomposition of PVC.<sup>18</sup> Although pentaerythritol could react with  $\text{ZnCl}_2$  to stop its catalysis, as shown in Reaction (3), their combination may be later than the catalysis of  $\text{ZnCl}_2$  begins.

The residues of PVC in the presence of stabilizers are higher than that of the pure PVC. The possible cause is that the introduction of penzinc or the mixture can bring more inorganic noncombustible residue. It is of interest to notice that PVC in the

**TABLE II**  
Values of Characteristics From TGA and DTG Curves

| Characteristics Materials | $T_s$ | $T_{\max 1}$ | $T_{\max 2}$ | $M_r$ |
|---------------------------|-------|--------------|--------------|-------|
| Pure PVC                  | 269.5 | 285.7        | 463.5        | 12.5  |
| PVC + 4 wt % mixture      | 262.3 | 280.4        | 462.9        | 20.1  |
| PVC + 2 wt % penzinc      | 275.8 | 293.0        | 461.5        | 14.4  |
| PVC + 4 wt % penzinc      | 270.3 | 286.4        | 464.6        | 17.1  |
| PVC + 6 wt % penzinc      | 264.3 | 285.6        | 464.1        | 18.4  |

presence of the mixture has the highest  $M_r$ , which may be attributed to the partially free  $ZnCl_2$  (the boiling point of  $ZnCl_2$  is  $732^\circ C$ ) formed at the early stage. In contrast, PVC with different ratios of penzinc shows lower residual mass ratio, suggesting coordination bond formed between Zn and O in pentaerythritol, thus no free  $ZnCl_2$  exists, which is in accordance with the aforementioned result from Congo Red test.

### CONCLUSION

Penzinc was successfully prepared via a solid-state reaction using ZnO and pentaerythritol in molar ratio of 1.4 : 1, and the reaction was characterized by TG-MS. The synthesis mechanism of penzinc proposed is that penzinc obtained through the dehydration between pentaerythritol and ZnO is likely to be a monopentaerythritol complex. The thermal stability test shows that the penzinc has excellent ability in absorbing HCl released in the degradation of PVC under heating. The  $T_s$  of the PVC containing penzinc was 38 min, much longer than the PVC with different commercially available thermal stabilizer. Furthermore, the PVC containing penzinc exhibits obvious enhancement of thermal stability. The Discoloration time has been extended to about 90 min. More importantly, no "zinc burning" has happened owing to the strong and stable coordination bond between zinc and oxide, and therefore no  $ZnCl_2$  was formed in the PVC containing penzinc. To sum up, penzinc is an excellent thermal stabilizer for rigid PVC.

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