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# Synergistic effects of lanthanum-pentaerythritol alkoxide with zinc stearates and with β-diketone on the thermal stability of poly(vinyl chloride)

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ABSTRACT

Lanthanum-pentaerythritol alkoxide (La-PE) was obtained by the traditional preparation method which was a reaction between $La_2O_3$ and pentaerythritol. The synergistic effects of La-PE with zinc stearates ($ZnSt_2$) and with stearoyl benzoyl methane (β-diketone) on the thermal stability of poly(vinyl chloride) (PVC) were evaluated by the conductivity test, thermal aging test, and Ultraviolet–visible (UV-VIS) spectroscopy test. The results showed an improvement on the color stability and the long-term thermal stability of PVC, indicating that there was an obvious synergistic effect between La-PE and $ZnSt_2$. In order to explore the mechanism, the capacity of La-PE to react with HCl was tested. The results showed that La-PE had lower capacity to neutralize HCl (80.30 mg HCl/1 g) than $ZnSt_2$ (92.71 mg HCl/1 g). Furthermore, the thermal stability test of PVC stabilized with La-PE/$ZnCl_2$ showed that the thermal stability of PVC with La-PE/$ZnCl_2$ was similar to that of PVC with La-PE/$ZnSt_2$ but better than PVC with pure La-PE. Thus, a possible synergistic mechanism of La-PE and $ZnSt_2$ could be described where zinc species could catalyze the reaction of La-PE and the labile chlorine atoms in PVC chains. Moreover, the hydroxyl group on La-PE could chelate $ZnCl_2$ to inhibit the "zinc burning" phenomenon. However, there was no synergistic effect observed between La-PE and β-diketone. Discoloration in PVC samples that stabilized with La-PE and β-diketone was noticed as early as in the milling process by the open twin-roller at 180 °C, even though it took 110 min for the reaction to change the color to completely black. The results of UV-VIS spectroscopy showed that a strong peak appeared at 360 nm representing the enol form of β-diketone when the dosage of β-diketone exceeded 1 phr. This indicated that the enol form of β-diketone did the work in the thermal stabilizing process and the dosage of β-diketone needed in the PVC stabilizers was very low.


## 1. Introduction

PVC heated to processing temperature in the absence of heat stabilizers degrades rapidly as it eliminates HCl. The degradation of PVC is an autocatalytic process; the acid catalyzes further elimination. In PVC the heat stabilizer functions both by neutralizing the HCl produced as the PVC thermally degrades and by repairing damage done to the polymer as successive chlorine atoms (chloride ions) are eliminated. Thermal stabilizers such as the commercial lead compounds and metallic soaps are used to prevent the degradation of PVC [1,2]. However, most of them are toxic; at present, non-toxic and environmentally friendly thermal stabilizers are becoming the focus of research. Zinc salts (e.g. zinc stearate) are efficient commercial thermal stabilizers for PVC, however they provide PVC heat stabilization only for a brief time as stabilized PVC is heated to processing temperature. As zinc chloride ($ZnCl_2$) builds

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up the stability of the PVC drops off rapidly. $ZnCl_2$ is a Lewis acid which catalyzes the dehydrochlorination of the PVC polymer [3]. Some auxiliary thermal stabilizers are used along with zinc salts to overcome this defect. The most common auxiliary thermal stabilizer is calcium stearate ($CaSt_2$). For example, when zinc stearate ($ZnSt_2$) and calcium stearate ($CaSt_2$) are used in combination, the $ZnSt_2$ reacts with HCl first briefly producing $ZnCl_2$ which then undergoes an exchange reaction with calcium stearate producing calcium chloride and $ZnSt_2$ [4]. Thus, the $ZnSt_2$ and $CaSt_2$ act synergistically to prolong the life of PVC at processing temperature. Although $CaSt_2$ and $ZnSt_2$ exhibit superior synergistic effect, auxiliary thermal stabilizers are still needed to be used together with $CaSt_2/ZnSt_2$ to inhibit the "zinc burning" phenomenon. Polyols, which can improve the initial color of the PVC and the thermal stabilizing efficiency of $CaSt_2/ZnSt_2$ stabilizers for PVC, are usually added as synergists to $CaSt_2/ZnSt_2$ stabilizing systems [5]. Pentaerythritol (PE) is one of the most important synergists for $CaSt_2/ZnSt_2$. There are two possible thermal stabilizing mechanisms of PE; it can form complexes with $ZnCl_2$ to delay the "zinc burning" [6] and it may react directly with HCl to remove the free HCl [7].

Many researchers have reported some studies about polyols, such as sorbitol, trimethylolpropane and dipentaerythritol which are used as additives to improve the long-term thermal stabilization [8,9]. Jenneskens et al. have reported the effect of the natural polyols on the thermal stabilization of PVC [10,11], and the results show that those natural polyols are efficient and benign co-stabilizers in stabilizer systems. However, the disadvantage of the $CaSt_2/ZnSt_2$/polyols system is its inefficiency in terms of long-term thermal stability.

In our team, we had synthesized metal alkoxides named pentaerythritol–zinc (Penzinc) [12] and pentaerythritol–Al (PE–Al) [13] which were used as PVC thermal stabilizers. The results showed that PVC stabilized with Penzinc and PE–Al separately had benign long-term thermal stability. Recently, we had synthesized a metal alkoxide named lanthanum-pentaerythritol alkoxide (La-PE) through heating the complexes of pentaerythritol and $La_2O_3$. Results of thermal stabilizing test showed that the addition of La-PE could significantly improve the long-term thermal stability of PVC. However, La-PE exhibited some weaknesses when used alone as a PVC heat stabilizer. In this study, the synergistic effects between La-PE and $ZnSt_2$, and between La-PE and β-diketone, which are the common additives to improve the initial color of PVC, were studied. The results showed that La-PE had significant synergistic effect with $ZnSt_2$. However, there is little synergistic effect between La-PE and β-diketone.

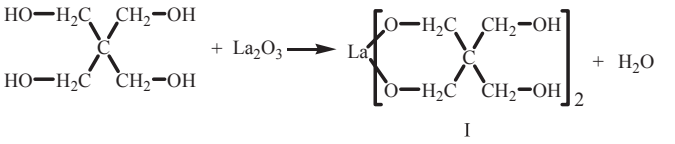
## 2. Experimental

### 2.1. Materials

PVC resin (average degree of polymerization: 1005, China Petrochemical Qilu Limited Company); zinc stearate ($ZnSt_2$, diameter is about 75 μm) and phenylicosane-1,3-dione (β-diketone) were supplied by Huike Additives Co., Ltd., Shandong, China. Pentaerythritol (PE), $La_2O_3$ and other chemical agents were all of analytical grade.

### 2.2. Preparation of La-PE

La-PE was prepared in the traditional method [14]. PE and $La_2O_3$ in a molar ratio of 4.5:1 were added into a mixer set and stirred for 4 min. Then the mixture and cyclohexane (used as water-carrying agent) were put into a three-necked flask equipped with an electrical blender and stirred vigorously at 190 ± 5 °C for 2 h. After having been dried in vacuum oven, the dry La-PE was ground in a grinder for 10 min at 4000 r/min. The diameter of the final La-PE was about 106 μm. The reaction equation is represented as below (Eq. (1)). The structure (I) is used to represent La-PE.




I

(1)

### 2.3. PVC-sample preparation

100.0 g of PVC, 2.0 g of acrylics copolymer (ACR), 20.0 g of $CaCO_3$, 4.0 g of $TiO_2$, 9.0 g of chlorinated polyethylene (CPE), 2.5 g of dioctyl phthalate (DOP) and 1.6 g of stearic acid (HSt) were added into a mixer set and dry blended to obtain the PVC master batch. Then 139.1 g of master batch and 4.0 g of thermal stabilizers were milled using an open twin-roller (XH-401, Dongguan Xihua Testing Machine Co., Ltd.) at 180 °C for 5 min. The thickness of compressed PVC sheet was about 1.0 mm.

### 2.4. Thermal stability test

#### 2.4.1. Conductivity measurement

The PVC sheets were cut into small squares of 0.2 mm × 0.2 mm with a total weight of 2 g, and put into the reaction vessels of the home-made thermal degradation device. The reaction vessels were placed in the heating blocks and heated at 180 °C. 240 mL distilled water was added into measuring vessels to detect the change of water conductivity. The schematic diagram of the conductivity test is described in Fig. 1. As shown in Fig. 1, the HCl gas formed from the dehydrochlorination reaction of PVC will be taken along by a nitrogen gas stream (about 7 L/h) and led into the measuring vessels. The HCl gas was absorbed by the distilled water in the measuring vessel, and the conductivity of the water changed with respect to time. Thus, we could monitor the decomposition rate of PVC by measuring the conductivity of aqueous solution [2]. A conductivity meter (DDS-307, Shanghai REX Instrument Factory, China) was used to measure the conductivity.

#### 2.4.2. Thermal aging test

The PVC sheet was cut into 10 mm × 10 mm pieces which were subjected to static thermal aging test in compliance with the ISO standard [15] via heat treatment at 180 °C in a thermal aging test box.

#### 2.4.3. UV-VIS spectroscopy test

It has been known that light and heat induce the dehydrochlorination reaction of PVC. The product of this reaction is an alkyl chain with conjugated double bonds which shows 7–10 absorption peaks in the range of 200–600 nm in UV-VIS spectra [16]. The UV-VIS spectroscopy of the PVC samples was recorded at 20 ± 1 °C using a UV-VIS spectrometer (UV-2450PC, Shimadzu Scientific Instruments, Japan) with the slit width set at 2.0 nm and 200–500 nm wavelength. Freshly distilled tetrahydrofuran was used as solvent.

Transfer 0.05 g of PVC sample and 60 mL of tetrahydrofuran to a 100-mL volumetric flask. After the PVC sample had been soaked for 72 h, the volumetric flask was vibrated for 10 min with the ultrasonic extractor and a little white flocculent residue was left in the solution. The solution was filtered and the residue was washed twice with tetrahydrofuran. All the filtrate was passed into another