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Effect of thermal stabilizers composed of zinc barbiturate and calcium stearate for rigid poly(vinyl chloride)

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ABSTRACT

Zinc barbiturate [$Zn(H_2L)_2 \cdot 2H_2O$, abbreviated as ZnL_2] was synthesized by a precipitation method in aqueous solution, and investigated as a co-stabilizer with calcium stearate ($CaSt_2$) for rigid poly(vinyl chloride) (PVC) by the discoloration test and the dehydrochlorination test at 180 °C. ZnL_2 exhibits high stabilizing effect with excellent initial colour of PVC films. In comparison with the synergistic effect of $CaSt_2/ZnSt_2$ stabilizers, the $CaSt_2/ZnL_2$ stabilizers in mass ratios ranging from 0.3/1.2 to 0.6/0.9 exhibit better synergistic effect. Moreover, PVC films stabilized by $CaSt_2/ZnL_2$ show better initial colour with the addition of dibenzoyl methane as an auxiliary stabilizer. The mechanism of stabilizing action of ZnL_2 is also proposed. ZnL_2 may replace the labile chlorine atoms to interrupt the formation of conjugated double bonds in PVC chains, and act as the absorber of hydrogen chloride to restrain the self-catalytic dehydrochlorination.

1. Introduction

Poly(vinyl chloride) (PVC) is a cost-effective and highly versatile polymer. However, PVC always undergoes severe thermal degradation at a relatively low temperature. The thermal degradation of PVC with dehydrochlorination leads to many problems, such as discoloration and the deterioration of mechanical properties. At present, proper stabilizers can be used to inhibit the thermal degradation of PVC during its thermal processing [1]. It is generally accepted that stabilizers can retard the thermal degradation of PVC in following ways: preventing the formation of conjugated double bonds through replacing the labile chlorine atoms in PVC chains, such as allylic and tertiary chlorine atoms; restraining the self-catalytic dehydrochlorination through the absorption of hydrogen chloride (HCl) released by the degradation of PVC [1–5].

Mixtures of calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$) are typical nontoxic thermal stabilizers for PVC. $CaSt_2$ causes long-term thermal stability in PVC by absorbing HCl, can lead to discoloration of PVC. In contrast, $ZnSt_2$ effectively inhibits discoloration by substituting labile chlorine atoms in the PVC chains, but gives a poor long-term stability [6,7]. An undesirable result of employing $ZnSt_2$ as a thermal stabilizer is the generation of zinc chloride ($ZnCl_2$), which may speed-up the degradation of PVC and result in a sudden “zipper dehydrochlorination” caused by its strong Lewis acidity [6,8]. Fortunately, $CaSt_2/ZnSt_2$ stabilizers in an appropriate ratio can exhibit good synergistic effects with both acceptable initial colour and long-term stability for PVC products [9–12].

Generally, the addition of auxiliary stabilizers including polyols [13–15] and β-diketones [16–19] into $CaSt_2/ZnSt_2$ stabilizers is necessary to obtain an improved stabilizing performance. For example, dibenzoyl methane (DBM) [17–19] one kind of β-diketone has been widely used as an auxiliary stabilizer to retard the decolouration of PVC. It is suggested that β-diketones can substitute the labile chlorine atoms through a C-alkylation reaction to prevent the discoloration of PVC. And β-diketones can act as an acceptor or chelating agent for metal chloride by forming an inert complex to retard the sudden “zipper dehydrochlorination” of PVC [16,17].

Hitherto, study on the zinc barbiturate [$Zn(H_2L)_2 \cdot 2H_2O$, abbreviated as ZnL_2)] as the thermal stabilizer for rigid PVC has not been reported, to the best of our knowledge. Mohamed et al. [20–22] reported that barbituric acid and some of its derivatives are efficient nontoxic organic stabilizers for rigid PVC. They proposed that barbituric acid exhibits thermal stabilizing efficiency through replacing labile chlorine atoms by the relatively stable moieties in the PVC chains. Hence, in the present study, it was of great interest to investigate the possibility of using ZnL_2 as the thermal stabilizer for rigid PVC. For convenient purposes, ZnL_2 was synthesized by precipitation method in aqueous solution, rather than in methanol [23].

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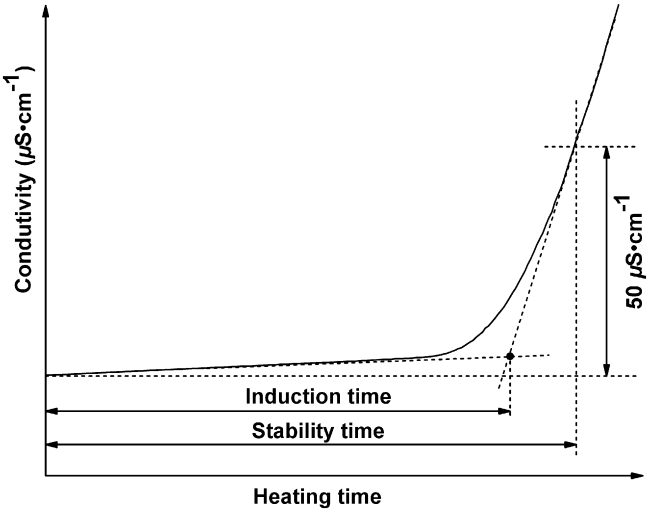

Fig. 1. Scheme of determination of the stability time and the induction time.

2. Experimental

2.1. Materials

The PVC (S-65) was purchased from the Formosa Plastics Corporation, Taiwan, China. Zinc barbiturate was synthesized by using barbituric acid (Zhengzhou Lifeng Chemical Corporation, China) and zinc acetate dihydrate (Sinopharm Chemical Reagent Company, China). Calcium stearate (Tianjin Fuchen Chemical Reagent Factory, China), zinc stearate (Aladdin Reagent, China) and dibenzoyl methane (Aladdin Reagent, China) were used as thermal stabilizers. Stearic acid (Tianjin Damao Chemical Reagent Factory, China) was employed as a lubricant.

2.2. Preparation and characterization of zinc barbiturate

ZnL_2 was prepared by the following procedure: Firstly, barbituric acid (38.43 g, 0.30 mol) was dissolved in 400 mL deionised water at 80 °C. Secondly, zinc acetate dihydrate (35.12 g, 0.16 mol) was added into the barbituric acid solution, and the mixture was stirred vigorously at 80 °C for 1 h. Thirdly, the precipitate was washed several times in deionised water until the pH of the filtrate reached 7.0. ZnL_2 was finally obtained by drying the precipitate at 80 °C for 12 h.

Carbon, hydrogen, oxygen and nitrogen contents of ZnL_2 were determined by a Vario EL III Elementar, and the content of zinc was measured by the HCl–HNO_3 pretreatment-EDTA complexometric titration. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of ZnL_2 were carried out at a heating rate of 10 °C min^{-1} from 50 to 500 °C under argon flow (50 mL min^{-1}) using a Mettler–Toledo TGA/DSC1 and a Mettler–Toledo DSC 823e, respectively. Fourier transform infrared (FTIR) spectra of ZnL_2 and barbituric acid were obtained on a Bruker Vertex70 infrared spectrophotometer by KBr disc method.

Table 1
Elemental analysis of zinc barbiturate.

Elements	%C	%H	% N	% O	%Zn
Calculated	27.0	2.83	15.8	36.0	18.4
Found	26.8	2.97	15.8	36.2	18.2

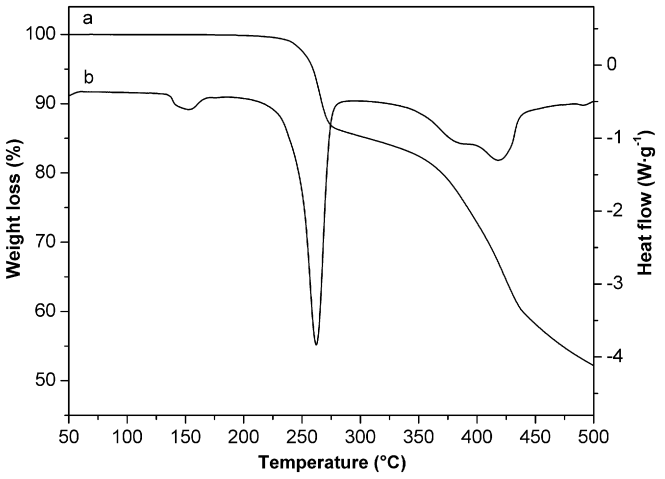

Fig. 2. TGA (a) and DSC (b) curves of zinc barbiturate.

2.3. Preparation and test of PVC films

PVC films were prepared using the following recipe: 50.00 g PVC resin stabilized by 1.50 g Ca/Zn ($CaSt_2/ZnSt_2$ or $CaSt_2/ZnL_2$) stabilizers (mass ratio: 1.5/0, 1.2/0.3, 0.9/0.6, 0.6/0.9, 0.3/1.2 and 0/1.5) in the absence and presence of DBM (0, 0.10 and 0.30 g), and 0.25 g stearic acid as lubricant. The PVC resin and additives were mixed thoroughly in a mortar, and the obtained mixtures were processed into rigid films with an approximate thickness of 0.5 mm on a two-roll mill (roll size: 35.0 cm in length, 12.0 cm in diameter; rotation speed of front/back roll: 24/30 rpm/rpm) at 170 ± 2 °C for 5 min.

The thermal stability of prepared PVC films was determined by the following two methods:

(a) Discoloration test. The PVC films were cut into about 4.5 cm × 3.0 cm strips and heated in a temperature-controlled oven at 180 ± 2 °C in air. Strips were removed every 10 min. The effect of the stabilizers was evaluated by the comparisons of visual colour differences of the heated PVC strips.
(b) Dehydrochlorination test. The rate of dehydrochlorination of PVC samples was measured at 180 °C on a Metrohm 763 PVC

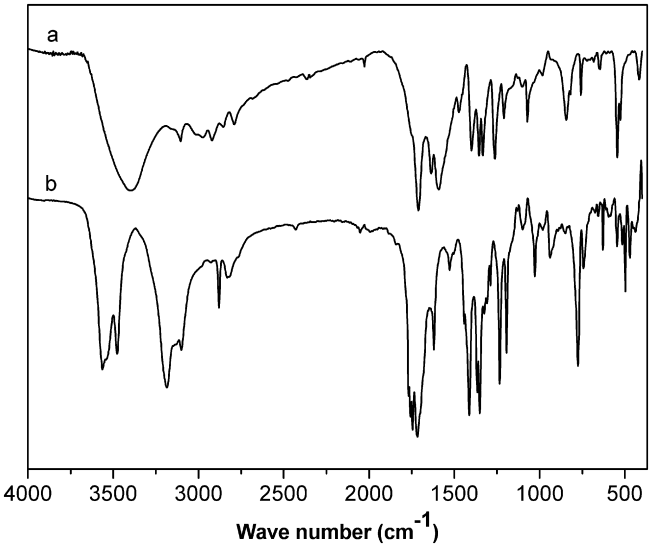

Fig. 3. FTIR spectra of zinc barbiturate (a) and barbituric acid (b).