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A novel zinc-containing additive for the long-term thermal stabilization of poly(vinyl chloride)

Guoan Chen, Liqiang Gu, Youwei Yao*

Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China

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ABSTRACT

A Zn-containing complex ($[ZnL_2]\cdot xH_2O$, $x \approx 4$, abbreviated as ZnL_2; HL = 1,3-dihydroxy-2-hydroxymethyl-2-(salicylidimino)propane) was synthesized and used as a thermal stabilizer. Through discoloration and dehydrochlorination tests at 180 °C, ZnL_2 was proved to be a co-stabilizer of long-term thermal stability for poly(vinyl chloride) (PVC): compared with the PVC samples stabilized using typical metallic soap stabilizers with the mass ratio of calcium stearate ($CaSt_2$) to zinc stearate ($ZnSt_2$) ranging from 1.5/0 to 0/1.5, whose induction time (t_i), stability time (t_s) respectively ranged from 9 to 54 min, from 12 to 56 min, the PVC samples stabilized using combinations with the mass ratio of $CaSt_2$ to ZnL_2 from 1.5/0 to 0/1.5 showed apparent thermal stability with t_i, t_s ranging from 44 to 85 min, from 49 to 88 min. PVC sample (PVC resin = 50.0 g, ZnL_2 = 1.5 g, pentaerythritol = 0.3 g, dioctyl phthalate = 2.5 g) displayed a significant long-term thermal stability with t_i of 102 min, t_s of 105 min, and totally-turning-black time of 170 min.

1. Introduction

It is well accepted that poly(vinyl chloride) (PVC) is one of the most commercial polymers. It is widely used due to its excellent properties [1,2]. However, PVC undergoes degradation during thermal processing, known as "zipper dehydrochlorination" [3]. The thermal degradation includes elimination of hydrogen chloride and formation of conjugated double bonds [4]. This process is followed by a change of PVC's color which goes gradually from white to yellow, orange, red, brown, and finally black [5–9]. This thermal degradation can also lead to a loss of mechanical properties [10]. The poor thermal stability of PVC is attributed to some defects in PVC chains such as allyl chlorine, tertiary chlorine [11]. Due to the poor thermal stability of PVC, thermal stabilizers are essentially used during its thermal processing [12,13].

According to the causes of the polymer's degradation, thermal stabilizers may contribute in at least one of the following ways: (1) substituting allyl chlorine or tertiary chlorine of PVC chains, removing the unstable factors of the polymer. These stabilizers are able to reduce early discoloration; (2) absorbing and neutralizing the self-catalyst, HCl, released during the degradation; (3) reacting with conjugated polyene sequences, blocking their further growth; (4) capturing free radicals [14–19].

Mixture of calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$) is a typical stabilizer due to their complementary effects. $ZnSt_2$ can substitute unstable chlorine atoms to ensure excellent initial whiteness of PVC. $CaSt_2$, in contrast, can lead to long-term thermal stability by absorbing and neutralizing HCl [20–23]. However, $ZnSt_2$ leads to the generation of $ZnCl_2$, which embodies strong Lewis acidity and may result in a sudden "zipper dehydrochlorination". Furthermore, although $ZnSt_2$ and $CaSt_2$ exhibit good stabilizing effects, higher efficiency of thermal stability is still needed.

Besides $CaSt_2$/$ZnSt_2$, some typical calcium- and zinc-containing stabilizers have been reported. For example, Egbuchunam et al. reported that a zinc soap of rubber seed oil (RSO) obtained through metathesis reaction can render a soft PVC sample stability time (t_s) of 3.87 h longer than those of two control samples (3.56 h, without stabilizer; 3.75 h, stabilized using 3 wt.% epoxidised rubber seed oil at 160 °C) [24]. For another example, Liu et al. found the difference in thermal stabilizing effectiveness among calcium or zinc glutarates, calcium or zinc sebacate [25]. Recently, Xu et al. reported that a basic zinc cyanurate complex can stabilize PVC sample with Congo Red paper discoloration time of 29 min, much longer than those of two control samples (7 min, without stabilizer; 15 min, stabilized using 2 phr mixture of $CaSt_2$ (50 wt.%) and $ZnSt_2$ (50 wt.%) at 180 °C). The stabilizing effect is suggestively attributed to absorbing and neutralizing HCl, and stabilizing the building units

* Corresponding author. Room 204A, Building J, Tsinghua Campus, The University Town, Shenzhen 518055, PR China. Tel./fax: +86 755 2603 6796.
E-mail addresses: yw_yao@yahoo.com, yaoyw@mail.tsinghua.edu.cn (Y. Yao).

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containing labile Cl atom through replacement reaction by cyanurate anion [26]. However, up to now, Zn salt that embodies long-term thermal stabilizing effectiveness for rigid or semi-rigid PVC has not been reported, to our knowledge.

In this study, a zinc complex ($[ZnL_2]\cdot xH_2O$, $x \approx 4$, HL = 1, 3-dihydroxy-2-hydroxymethyl-2-(salicylidimino) propane, abbreviated as ZnL_2) was investigated as a co-stabilizer, together with $CaSt_2$, for stabilizing PVC. The stabilizers of $CaSt_2/ZnL_2$ showed higher stabilizing effectiveness than $CaSt_2/ZnSt_2$ in both discoloration and dechlorination tests. Especially, as a long-term stabilizer, ZnL_2 rendered PVC sample totally-turning-black time of 170 min in the presence of pentaerythritol.

2. Experimental

2.1. Materials

Commercial PVC S-65 with a *K* value of 64.6–66.0 was purchased from Formosa Plastics Corporation, (China). Tris(hydroxymethyl)aminomethane from Cantotech (China), salicylaldehyde from Aladdin Reagent (China), zinc acetate dihydrate from Aladdin Reagent (China), calcium stearate from Tianjin Fuchen Chemical Reagent Factory (China), zinc stearate from Aladdin Reagent (China), pentaerythritol (PER) from Sinopharm Chemical Reagent (China), dibenzoyl methane (DBM) from Aladdin Reagent (China), epoxidized soybean oil (ESBO) from Shanghai Wenhua Chemical (China), Ethanol from Damao Chemical Reagent Factory (China), and nitrogen gas from Shenzhen Chuanglantian Chemical (China) were of the analytical reagent grade (AR) and were used without purification.

2.2. Preparation and characterization of Schiff base ligand HL and its complex ZnL_2

The Schiff base, 1,3-dihydroxy-2-hydroxymethyl-2-(salicylidimino)propane (abbreviated as HL) was synthesized in a typical method using tris (hydroxymethyl)aminomethane and salicylaldehyde [27–29]. HL was prepared by adding equal molar of tris(hydroxymethyl)aminomethane (2.42 g, 20 mmol) and salicylaldehyde (2.44 g, 20 mmol) in 100 mL absolute ethanol under nitrogen atmosphere with stirring for 2 h at 40 °C, and then a yellow solution was obtained. HL was recovered by concentrating the yellow solution, and filtering and washing the yellow solid product using ethanol for three times.

The HL (2.35 g, 10 mmol) was dissolved in 50 mL absolute ethanol and zinc acetate (1.10 g, 5 mmol) was added to the solution of HL. The reaction mixture was stirred at 50 °C for 3 h. The resulting precipitate ZnL_2 was filtered off and washed with cold ethanol.

Carbon, hydrogen, and nitrogen contents of ZnL_2 were determined using a Vario EL III Elementar, and the content of zinc was measured on an ICP-OES. Both thermal gravimetric analysis (TGA) of HL and 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. Fourier transform infrared (FTIR) spectra of HL and ZnL_2 were obtained on a Bruker Vertex70 infrared spectrophotometer by KBr disc method. ^{1}HNMR analysis was carried out with a Bruker AV-400 spectrometer using DMSO-d6 as a solvent and TMS as an internal standards.

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 $CaSt_2/ZnL_2$ 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, PER, ESBO, and 2.5 g dioctyl phthalate (DOP) as the lubricant and plasticizer. The PVC resin and additives were mixed thoroughly in a mortar, and the obtained mixtures were processed into films with an approximate thickness of 0.5 mm on an open KY-3203 two-wheel mill (roll size: 35.0 cm in length, 12.0 cm in diameter; rotation speed of front/back roll: 24/30 rpm/rpm) at 180 ± 2 °C for 5 min.

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

(a) Discoloration test. The resulting PVC sample sheets with a thickness of 1.0 mm were cut into about 3.0 cm × 2.0 cm strips and heated in a temperature-controlled oven at 180 ± 2 °C in air. Strips were removed out of the oven every 10 min. The effect of the stabilizers was evaluated by the comparisons of visual color differences of the heated PVC strips. The time for sample totally-turning-black is recorded as "zinc burning time".

(b) Dehydrochlorination test. The rate of dehydrochlorination of PVC samples was measured at 180 °C on a Metrohm 763 PVC thermomat described in detail elsewhere [16]. 0.50 g of PVC films with a size of about 2.0 mm × 2.0 mm were placed in the reaction vessel. And the gaseous HCl released from the degradation of PVC samples was blew by nitrogen gas (7.0 L h^{-1}). According to the German standard DIN 53381-1, the efficiency of thermal stabilizers was evaluated by stability time and induction time.

3. Results and discussion

3.1. Characterization of HL and ZnL_2

Elemental analysis for HL (Calc. C: 58.86%, H: 6.78%, N: 6.20%, Exp. C: 58.66%, H: 6.71%, N: 6.22%), together with FTIR spectra (see below), is in well agreement with that of Schiff base reported previously [29]. The elemental analysis for ZnL_2 (Calc. C: 45.10%, H: 6.19%, N: 4.78%, Exp. C: 45.27%, H: 6.24%, N: 4.81%) indicates that the ratio of metal to ligand stoichiometry for ZnL_2 is 2:1. Compared with the similar Schiff base–zinc complex, $ZnL_2\cdot(CH_3OH)$, synthesized by Dey et al. [28], the zinc complex prepared in our experiment is not methanolated. By calculating the content of remaining H element of ZnL_2, the complex is tetrahydrated. The number of combined water is in accordance with the TGA result (see below). This tetrahydrated zinc complex has a zinc content of 11.16%

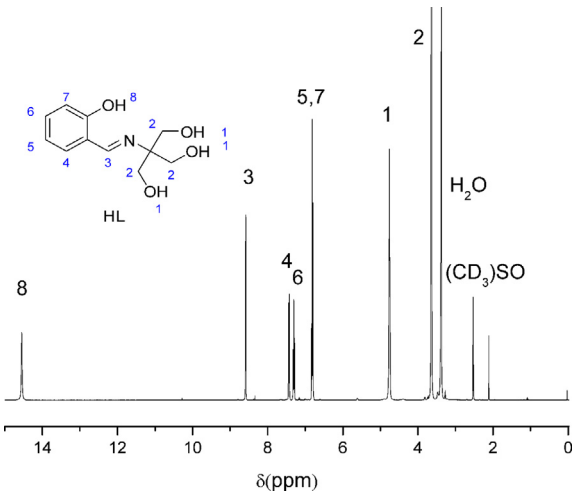

Fig. 1. ^{1}H NMR spectrum of HL.