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Investigation of basic zinc cyanurate as a novel thermal stabilizer for poly(vinyl chloride) and its synergistic effect with calcium stearate

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ABSTRACT

Basic zinc cyanurate ($Zn_3(C_3N_3O_3)_2{\cdot}ZnO$, represented as Zn_3Cy_2) was synthesized via a precipitation method, and investigated as a thermal stabilizer for poly(vinyl chloride) (PVC) by thermogravimetric analysis (TGA), Congo red test and discoloration test. The thermal stability of PVC was significantly enhanced with the addition of Zn_3Cy_2. Compared with zinc stearate ($ZnSt_2$), it is observed a significant improvement that Zn_3Cy_2 could delay the "zinc burning" of PVC. This is attributed to the strong ability of the cyanurate anions in Zn_3Cy_2 to absorb the hydrogen chloride released by the degradation of PVC. Moreover, mixing Zn_3Cy_2 with calcium stearate ($CaSt_2$) in different mass ratios greatly promoted the thermal stability of PVC. Excellent synergistic effects could be observed when $CaSt_2/Zn_3Cy_2$ combined with some commercial auxiliary stabilizers. Addition of dibenzoylmethane (DBM) brought a remarkable increase in initial color for PVC containing $CaSt_2/Zn_3Cy_2$ while epoxidized soybean oil (ESBO) could improve both initial color and long-term stability.

1. Introduction

Poly(vinyl chloride) (PVC), one of the most important commercial thermoplastics, undergoes severe degradation at processing temperature resulting in deterioration of properties [1–3]. The degradation can be prevented with thermal stabilizers that must perform at least two basic functions: absorption of hydrogen chloride (HCl) released by the degradation of PVC and replacing the labile chlorine atoms in PVC chains, such as allylic and tertiary chlorine atoms [4–6].

During the past several decades, various kinds of compounds have been investigated as PVC stabilizers, among which metal soaps [7], lead salts [8], and organotin [9] are prominent. Although lead salts and organotin have high efficiency to stabilize PVC, these stabilizers are restricted owing to their toxicity [10]. Recently, Ca/Zn thermal stabilizers (Ca/Zn), the most used metal soaps, are playing more and more important roles in this field because of its nontoxic [11,12]. However, an undesirable product formed from Ca/Zn in PVC is zinc chloride ($ZnCl_2$), which may catalyze the degradation of PVC and result in a sudden "zipper dehydrochlorination" caused by its strong Lewis acidity [13]. As a consequence, it is of interest to explore novel zinc-based stabilizers with high efficiency and have no positive catalytic effects on the degradation of PVC. Zinc barbiturate investigated by Shumin Li and Youwei Yao [14], showed good efficiency and exhibited synergistic effect with dibenzoylmethane in stabilizing PVC. Shilu Xu et al. [15] reported the synthesis of pentaerythritol-zinc, and studied its efficiency to stabilize rigid PVC. They stated that PVC containing pentaerythritol-zinc exhibited obvious enhancement of thermal stability and had no "zinc burning" effect in the stabilizing reaction.

On the other hand, pyrimidinedione derivatives, which were briefly reviewed by Starnes and coworkers [16], acted as excellent stabilizers for PVC and had been commercialized in past few years. Santamaria et al. [17] found that pyrimidinedione derivatives could take place via substitution of labile chlorines by N-alkylation reaction, stopping the growth of the polyene sequences in PVC chains. Moreover, a combination of pyrimidinedione derivatives and zinc stearate ($ZnSt_2$) was proved to be desirable efficiency in improving the long-term stability of PVC in our previous study [18]. Thus, in view of some structural similarity of cyanuric acid to pyrimidinedione, the objective of this work is to investigate the possibility of using basic zinc cyanurate ($Zn_3(C_3N_3O_3)_2{\cdot}ZnO$, represented as Zn_3Cy_2) as a thermal stabilizer for PVC.

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2. Experimental

2.1. Materials

PVC (SG-5, polymerization temperature: 55 °C, average degree of polymerization: 1000) used in this work was purchased from Xinjiang Tianye (Group) Co. Ltd., China. Calcium stearate ($CaSt_2$, calcium content: 6.6–7.4%), zinc stearate ($ZnSt_2$, zinc content: 10–12%) and dioctyl phthalate (DOP, C.P.) were obtained from Zhejiang Himpton New Material Co. Ltd., China. Ca/Zn thermal stabilizers (Ca/Zn) were consisted of $CaSt_2$ (50 wt%) and $ZnSt_2$ (50 wt%). Dibenzoylmethane (DBM, A.R.), epoxidized soybean oil (ESBO, C.P.), lead subacetate (LSA, A.R., molecular formula: $Pb(CH_3COO)_2 \cdot 2PbO \cdot 2H_2O$) were purchased from Aladdin Reagent, China. Other chemical reagents used in this study are of analytical grade.

2.2. Preparation and characterization of Zn_3Cy_2

Zn_3Cy_2 was prepared according to the following methods: cyanuric acid (2.58 g) and anhydrous zinc acetate (6.80 g) were dissolved in 100 mL deionized water in a 250 mL three-neck flask with a magnetic stirrer, a condenser and a dropping funnel. The three-neck flask was heated to 80 °C in an oil bath. Then, 62 mL NaOH aqueous solution (1.0 mol/L) was added dropwise over 1 h and the mixture was stirred for another 1 h. After the reaction, the resultant solid was separated by filtration, washed with deionized water and dried in a vacuum desiccator at 55 °C.

Zinc content of Zn_3Cy_2 was measured with using xylenol orange as indicator by EDTA titration, and the atomic concentration ratio of zinc to nitrogen was determined by X-ray Photoelectron Spectroscopy (XPS) (AXIS Ultra DLD, KRATOS, Japan). Fourier transform infrared (FTIR) spectra of Zn_3Cy_2 and cyanuric acid were recorded on a FTIR spectrophotometer (Nicolet 6700, Thermo Fisher Scientific Inc., USA) by KBr disc method. Thermal degradation of Zn_3Cy_2 were measured on a thermogravimetric analyzer (TGA) (SDT Q600, TA Instruments., USA) from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The non-isothermal melt-crystallization behavior of the synthesized Zn_3Cy_2 was investigated using a differential scanning calorimeter (DSC) (Q100, TA Instruments., USA) under nitrogen atmosphere. The surface morphology of the Zn_3Cy_2 coated with a thin layer of palladium gold alloy was observed using a Scanning electron microscope (SEM) (S-4700, Hitachi Ltd., Japan) with an acceleration voltage of 15 kV.

2.3. Preparation of PVC samples

Mixtures containing PVC resin, DOP, $CaCO_3$ and stabilizers were mixed on an open twin-wheel mill (LRM-S-150/3E, Labtech Ltd., Sweden) for 5 min at 180 °C. The resulting compositions were compressed to sheets with a thickness of 1.0 mm at 120 bar and 190 °C in a scientific laboratory hydraulic press (LP-S-50, Labtech Ltd., Sweden). The thermal stability of prepared PVC sheets was determined by discoloration test and thermogravimetric analysis.

2.4. Evaluation of stabilizing efficiency

2.4.1. Congo red test

PVC was mixed with 2 phr stabilizers in the mortar, and then they were put into a tube with Congo red test paper located at 2 cm above the sample. The tube was immersed into an oil bath at 180 °C in air for evaluating static thermal stability of PVC composites. The static thermal stability time (T_s) was defined as the time when the Congo red paper began to turn to blue.

2.4.2. Discoloration test

The PVC sheets were cut into about 30 mm × 20 mm strips and heated in a temperature-controlled oven (DHG-9140A, Shanghai Yiheng Scientific instruments Co.,Ltd., China) at 180 °C in air. Strips were taken out of the oven every 10 min and subjected to visual examination using a scanner (Bizhub 283, Konica Minolta, Int. Japan). The effect of the stabilizers was evaluated by the comparison of visual color differences of the heated PVC strips.

2.4.3. Thermogravimetric analysis

Thermal degradation of the PVC sheets were measured on a thermogravimetric analyzer (SDT Q600, TA Instruments., USA) from room temperature to 700 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

2.5. Investigation of mechanism of Zn_3Cy_2 as a thermal stabilizer for PVC

The following two experiments were performed to investigate the mode of action of Zn_3Cy_2 as a thermal stabilizer for PVC. Zn_3Cy_2 was subjected to a stream of dry HCl gas at 180 °C in air for 2 h, and the product was heated at 120 °C in air for 4 h to remove the residual HCl. Then the treated product was added into deionized water, and the relevant mixture was filtered. Finally, one droplet of 0.1 N silver nitrate solution was added in to determine whether the filtrate contained chloride ions, and further confirm whether Zn_3Cy_2 could act as the HCl absorber.

Another experiment was performed to investigate whether Zn_3Cy_2 could replace the labile chlorine atoms in PVC chain. The Zn_3Cy_2 stabilized PVC was mixed on an open twin-wheel mill (LRM-S-150/3E, Labtech Ltd., Sweden) for 10 min at 180 °C. Then Zn_3Cy_2 stabilized PVC was dissolved in tetrahydrofuran and the mixture was separated by filtration to remove the unreacted Zn_3Cy_2. Finally, the PVC sample was precipitated with methanol and collected by filtration. This purified sample after aging at 180 °C in air for different time intervals (from 10 to 30 min) was characterized with FTIR spectra.

3. Results and discussion

3.1. Characterization of Zn_3Cy_2

Cyanuric acid is a tribasic acid so it will be understood that the zinc cyanurate prepared in alkaline system in our laboratory was the basic salt. The XPS analysis results of Zn_3Cy_2 indicated that the atomic concentration ratio of zinc to nitrogen is 40.6:59.4, and the zinc content of Zn_3Cy_2 obtained by EDTA titration was 51.3%. Therefore, we deduce that the molecular formula of this product is $Zn_3(C_3N_3O_3)_2 \cdot ZnO$ (calculated value for zinc content is 49.2%). In this article, Zn_3Cy_2 is used to represent $Zn_3(C_3N_3O_3)_2 \cdot ZnO$.

The thermal behavior of Zn_3Cy_2 was characterized by TGA at heating rate of 10 °C/min. As is shown in Fig. 1, the TGA curve of Zn_3Cy_2 shows a little weight loss at the temperature range from 25 to 300 °C which is assigned to the absorbed water [11]. It can also be seen from the curve that further decomposition of Zn_3Cy_2 occurred over 310 °C in two steps. The first weight loss step within the temperature range of 310–490 °C could be attributed to the release of three molecules of carbon monoxide with an estimated mass loss of 15.1% (calcd. 15.9%). The second mass loss step 21.3% occurred in the range of 490–800 °C, due to the decomposition of the rest of cyanurate anion (calcd. 22.7%) leaving ZnO as a residue 63.4% (calcd. 61.4%). On the other hand, it can be found that Zn_3Cy_2 is relatively stable at temperature up to 200 °C with a weight loss less than 1%. The results reveal that Zn_3Cy_2 is stable at the processing temperature range of 160–200 °C in PVC system.

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