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Efficiency and mechanism for the stabilizing action of *N,N'*-bis(phenylcarbamoyl)alkyldiamines as thermal stabilizers and co-stabilizers for poly(vinyl chloride)

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ABSTRACT

A series of novel ureido organic stabilizers for poly(vinyl chloride) (PVC) with different length of alkyl chains, including *N,N'*-bis(phenylcarbamoyl)ethylenediamine (NA2), *N,N'*-bis(phenylcarbamoyl)butylenediamine (NA4) and *N,N'*-bis(phenylcar- bamoyl)hexamethylenediamine (NA6) were designed and synthesized, which have greater stabilizing efficiency compared with Ca/Zn stabilizers and phenylurea at the same concentration in PVC mixtures. The results of Congo red test, discoloration test, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectra showed that the ureido moieties of NAn ($n = 2, 4, 6$) have stronger ability to replace the labile chlorine atoms in PVC chains, but weaker ability to absorb hydrogen chloride (HCl) than those in phenylurea. On the other hand, longer alkyl chains in the synthesized organic stabilizers had positive effect in stabilizing efficiency for PVC, which was proved by the results that NA6 was the most efficient stabilizer among the present study, followed by NA4 and NA2. Furthermore, mixing the model compound NA6 with zinc stearate in different mass ratios led to a true synergistic effect, the "zinc burning" of PVC products was remarkably postponed.
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1. Introduction

As the most important additives for poly(vinyl chloride) (PVC), thermal stabilizers must be incorporated to restrain the thermal degradation resulted from inherent structural defects in the polymer chains during thermal processing [1–4]. It is generally accepted that thermal stabilizers realize the thermal stability mainly through absorption of hydrogen chloride (HCl) released by the degradation of PVC or reacting with the labile chlorine atoms, such as allylic and tertiary chlorine atoms [5–7]. At present, the main commercial stabilizers used for PVC include lead salts [8], organotin compounds [9], metal soaps [10], and organic stabilizers [11]. Although lead salts and organotin compounds have high efficiency to stabilize PVC, they are restrained due to their toxicity. In respect of the increasing public awareness of environmental issues in the world, the performance contribution of metal soaps and organic stabilizers has become increasingly important [12,13].

Urea derivatives have been widely investigated as organic stabilizers for PVC during the last few decades [14–16]. However, application of urea derivative stabilizers is limited because of their low efficiency. Hence, the attention of many investigators has been focused on exploring new kinds of urea derivative stabilizers which can meet the demands of PVC industry. A series of phenylurea and phenylthiourea derivatives developed by Sabaa et al. [17–19], revealed high stabilizing potency for PVC and led to a true synergistic effect with metal soaps. Uracil derivatives, which could be synthesized using urea derivatives as raw materials, have been proved to be effective additives for stabilization of PVC against thermal degradation in our previous study [20].

Herein, a class of *N,N'*-bis(phenylcarbamoyl)alkyldiamines (NAn, $n = 2, 4, 6$) were synthesized, characterized and investigated as novel organic thermal stabilizers for PVC. The influence of the alkyl chain length of these compounds on stabilizing efficiency for PVC was investigated and the results suggested that longer alkyl chains had positive effect in stabilizing efficiency for PVC. In addition, by using them as co-stabilizers with zinc stearate, they had special postponing "zinc burning" effect of PVC products through reacting with the zinc chloride. Congo red test, discoloration test, thermogravimetric analysis (TGA) and Fourier transform infrared

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(FTIR) spectra were used to systematically discuss the mechanism for the stabilizing action of the synthesized organic stabilizers.

2. Experimental

2.1. Materials

PVC (SG-5, 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.) and $CaCO_3$ (1000 mesh) were supplied by Zhejiang Himpton New Material Co. Ltd., China. $CaSt_2/ZnSt_2$ thermal stabilizers (Ca/Zn) consisted of $CaSt_2$ (50 wt%) and $ZnSt_2$ (50 wt%). Phenylurea (PU, A.R.) was purchased from Aladdin Reagent, China. Other chemical reagents used in this study are of analytical grade.

2.2. Preparation of N,N′-bis(phenylcarbamoyl)alkyldiamines

N,N′-bis(phenylcarbamoyl)alkyldiamines were all prepared according to the following methods: phenylurea (5 mmol) and alkyldiamines (10 mmol) were dissolved in 25 mL 1,4-dioxane in a 100 mL round-bottomed flask, equipped with a magnetic stirrer and a thermometer. The mixture was then stirred and heated to reflux for about 24 h under an argon atmosphere. After the reaction, the resultant solid was separated by filtration, washed with deionized water, recrystallized using methanol, and dried in a vacuum desiccators at 50 °C for 12 h.

2.3. Characterization

^{1}H-NMR spectra of the synthesized stabilizers were measured on an ANANCEIII (500 MHz) spectrometer (Bruker Corporation, Switzerland), using DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard.

Mass spectra of the synthesized stabilizers were recorded on a 6210 TOF LC/MS mass spectrometer (Agilent, USA) by positive mode electrospray ionization.

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

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific Inc., USA) by KBr disc method.

2.4. Preparation of PVC samples

PVC resin (100 phr), DOP (15 phr), $CaCO_3$ (10 phr) and stabilizers (2 phr) were mixed thoroughly in a mortar, and the obtained compound was processed into sheets with an approximate thickness of 1.0 mm on an open twin-wheel mill (LRM-S-150/3E, Labtech Ltd., Sweden) for 5 min at 180 °C. The thermal stability of prepared PVC sheets was determined by discoloration test and thermogravimetric analysis.

2.5. Evaluation of stabilizing efficiency

2.5.1. Congo red test

The PVC compound mixed with 2 phr stabilizers in the mortar was 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 compound. The static thermal stability time (T_s) was defined as the time when the Congo red paper began to turn to blue.

2.5.2. 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.

2.5.3. 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.

3. Results and discussion

3.1. Characterization of NAn

The structures of NAn were identified by ^{1}H-NMR spectra and mass spectra.

N,N′-bis(phenylcarbamoyl)ethylenediamine (NA2, as shown in Fig 1): White solid, yield: 75%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a = 3.19(t, 4H), δ_b = 6.19 (s, 2H), δ_f = 6.88(t, 2H), δ_e = 7.19(t, 4H), δ_d = 7.38(d, 4H), δ_c = 8.52(s, 2H). MS *m/z*: 299.1$[M + H]^+$, *m/z*: 321.1 $[M + Na]^+$.

N,N′-bis(phenylcarbamoyl)butylenediamine (NA4, as shown in Fig 2): White solid, yield: 61%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a = 1.45(s, 4H), δ_b = 3.11 (d, 4H), δ_c = 6.13(t, 2H), δ_g = 6.88(t, 2H), δ_f = 7.19(t, 4H), δ_e = 7.38(d, 4H), δ_d = 8.37(s, 2H). MS *m/z*: 327.2 $[M + H]^+$, *m/z*: 349.2 $[M + Na]^+$.

N,N′-bis(phenylcarbamoyl)hexamethylenediamine (NA6, as shown in Fig 3): White solid, yield: 54%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a = 1.45(s, 4H), δ_b = 3.09 (d, 4H), δ_c = 6.13(t, 2H), δ_g = 6.87(t, 2H), δ_f = 7.21(t, 4H), δ_e = 7.37(d, 4H), δ_d = 8.37(s, 2H). MS *m/z*: 355.2 $[M + H]^+$.

The thermal behavior of the synthesized stabilizers at a constant heating rate of 10 °C/min was characterized by TGA. The temperature of the rapidest decomposition (T_{rpd}) and residue yield at 200 °C obtained for these stabilizers are summarized in Table 1. As listed in Table 1, all of the synthesized stabilizers are relatively stable at temperature up to 200 °C with a weight loss less than 0.4% and the T_{rpd} occurred over 240 °C. The results reveal that NAn are stable at the processing temperature range of 160–200 °C in PVC system and therefore could be used as thermal stabilizers for PVC.

3.2. Thermal stability of NAn stabilized PVC

Results of the thermal stability against the dehydrochlorination process of PVC containing NAn evaluated by Congo red test are shown in Fig. 4. The results of PVC samples stabilized by Ca/Zn stabilizers (Ca/Zn) and phenylurea (PU) used as reference stabilizers are also given for comparison. It is seen that these three investigated organic stabilizers exhibit similar stabilizing efficiency

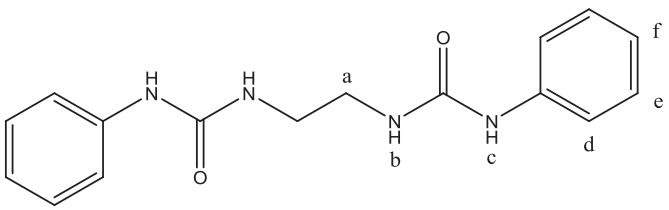

Fig. 1. Structure of *N,N′*-bis(phenylcarbamoyl)ethylenediamine (NA2).

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