

Zinc Glycerolate with Lanthanum Stearate to Inhibit the Thermal Degradation of Poly(vinyl chloride)

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ABSTRACT: Zinc glycerolate (ZnGly) was prepared and used as a poly(vinyl chloride) (PVC) thermal stabilizer in this work. ZnGly was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetry (TGA), and transmission electron microscopy (TEM). Visual color evolution and thermal stability time at 180°C were used to examine the stabilizing efficiency of the samples. The thermal stability of PVC was significantly enhanced through adding ZnGly or ZnGly with lanthanum stearate (LaSt₃). Compared with zinc stearate (ZnSt₂), it was demonstrated the initial color stability was markedly improved and the thermal stability time was obviously extended by adding ZnGly. The thermal stability time of ZnGly was threefold than ZnSt₂. In comparison with CaSt₂/ZnSt₂, the extent of coloration of PVC samples was significantly inhibited though adding LaSt₃/ZnGly. It was verified that the appropriate percents of ZnGly in the mixture were between 25 and 50%. A possible mechanism for the stabilizing efficiency of ZnGly was also proposed. The stabilizing efficiency was attributed to the stabilizer's ability to absorb hydrogen chloride and replace the labile chlorine atoms on PVC chains. Moreover, the dynamic thermogravimetric analysis was used to confirm that combination of LaSt₃ with ZnGly presented an obvious improvement of stability on thermal degradation of PVC. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: poly(vinyl chloride); stabilization; degradation; zinc glycerolate; lanthanum stearate

Received 30 August 2011; accepted 27 April 2012; published online

DOI: 10.1002/app.37985

INTRODUCTION

Poly(vinyl chloride) (PVC) resins are widely used as thermoplastic polymer because of versatility and low cost.¹ However, PVC is less stable than many other thermoplastics and degraded by the effect of heat, oxygen, light, and mechanical energy.^{2,3} It is generally accepted that dehydrochlorination reaction with progressively increasing numbers of double bonds results in changing of material color, structure degradation, and properties deterioration.⁴ Appropriate stabilizers must be incorporated to restrain the degradation of PVC during mechanical hot-working. Ca/Zn thermal stabilizers with high synergistic effects are nontoxic according to relevant literatures.^{5–9} Calcium carboxylate and zinc carboxylate are widely used. However, zinc carboxylate can produce ZnCl₂ which can promote a sudden dehydrochlorination of PVC during the stabilization process.¹⁰ A recent study on the interaction between calcium carboxylate and zinc carboxylate system has been demonstrated. In their work, the percentage of the zinc compound in the mixture with

costabilizer (calcium stearate or pentaerythritol) should be <20%.⁸ The increasing percentage of the zinc carboxylate in the mixture decreases the time of PVC changing into black. Nonetheless, zinc carboxylate can inhibit the initial coloring. It is necessary to explore new materials used as thermal stabilizers of PVC for inhibiting the initial coloring and improving the long-term stability. Zinc glycerolate (ZnGly), is widely used in light stabilizer of plastic and rubber because of its nontoxicity and the excellent ability in fighting against ultraviolet.^{11–13} Meanwhile, glycerol, the by-product of biodiesel production, is renewable resource and low cost. Until now, there are few reports about the thermal stability of ZnGly on PVC.^{11,14}

As a costabilizer, the rare earth thermal stabilizer has many advantages, such as long-term stabilization effect, nontoxic, and good synergetic effect with other stabilizers.^{15–18} The rare earth thermal stabilizer owns outstanding stabilization because the rare earth ion can absorb HCl effectively and react with the labile chlorine atom yielding a stable complex. However, the rare

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earth stabilizer usually exhibits poor initial stabilization effect, which needs to combine with other stabilizers such as organotin and organic zinc to improve the thermal stabilization.¹⁹

In this work, effects of ZnGly and lanthanum stearate (LaSt₃) on the thermal stability of PVC were discussed. Impacts of ZnGly on restraining the blackening time of PVC and long-term stability were also investigated. Meanwhile, kinetic parameters of the thermal degradation of blank PVC, PVC containing ZnGly, and PVC containing LaSt₃/ZnGly were obtained from the dynamic TG curves.

EXPERIMENTAL

Materials

The PVC (SG-5, the average degree of polymerization: 1000) resin was supplied by Hangzhou Chuanhua. DOP, zinc oxide (ZnO), glycerol, stearic acid, sodium hydroxide, and lanthanum chloride were purchased from Sinopharm Chemical Reagent. Calcium stearate (CaSt₂) and zinc stearate (ZnSt₂) were obtained from Italy FACI.

Synthesis of ZnGly and LaSt₃

ZnO (3.00 g) was added to glycerol (30 g) and the mixture was refluxed for 5 h at 120°C under moderate stirring. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 150°C for 18 h. After cooling to room temperature, the resultant mixture was filtered, washed with distilled water and ethanol, and dried at 100°C for 12 h.

LaSt₃ was prepared by double decomposition method.²⁰ Stearic acid (10 g) was added to 120 cm³ of distilled water and the mixture was heated to 90°C under stirring. Then sodium hydroxide (1.43 g) was dissolved into the stearic acid solution to saponification. The mixture was stirred at 90°C for 30 min and the right amount of LaCl₃ solution was dripped. The obtained mixture was filtered, washed with distilled water, and dried at 110°C to a constant weight.

Characterization for ZnGly

The elemental analyses data for the prepared product were performed using an elemental analyzer Vario EL III of German Elementar. Atomic absorption was done on Spectr AA 220/220Z to determine the amount of zinc ions existed in the ZnGly. FT-IR experiments were performed on a spectrophotometer NICOLET NEXUS 470 FT-IR in the range of 4000–510 cm⁻¹. The samples were characterized at different scales/magnifications by transmission electron microscopy (TEM) (JEM-2100, Jeol) operated at 200 kV. The X-ray diffraction (XRD) of powder samples were examined by X-ray diffraction studies (Bruker) using Cu K α ($\lambda = 0.15406$ nm), operated at 40 kV and 40 mA at a scan rate of 4° min⁻¹ in the two theta range 5°–80°. The thermogravimetric analysis (TGA) of samples was determined with the TGA/DSC1/1100 SF thermal-analysis instrumentation (Mettler Toledo, Switzerland). Thermal decomposition behaviors were collected by TGA studies in 50 cm³ min⁻¹ nitrogen gas with a temperature increase rate of 20°C min⁻¹.

Preparation of PVC Samples

PVC samples for static oven test and evaluation of stabilization efficiency were prepared by thoroughly mixing 100 phr PVC, 50

phr (per hundred resin) DOP, and 2 phr stabilizer (or a mixed stabilizer) at 25°C. The mixture was placed in the glass template with the thickness of 1.0 ± 0.1 mm, gelation at 120°C for 20 min. Then samples were taken out from glass template after cooling to room temperature. PVC samples for thermogravimetric analysis were prepared by perfectly mixing 100 phr PVC and 3 phr stabilizer (or a mixed stabilizer) in a mortar and the resulting mixed powder was used in the evaluation.

Procedure for Thermal Stability

Static Oven Test. PVC resin (100 phr), DOP (50 phr), and the stabilizer (2 phr) were made into sheets. The sheets with dimensions of 15 mm × 15 mm × 1 mm were placed in a circulating air oven maintained at 180.0°C ± 1.0°C. PVC samples were examined visually every 10 min.

Evaluation of Stabilization Efficiency. According to the standard of ASTM D4202, evaluation of the stabilization efficiency for stabilizers was carried out by using Congo red paper method to measure the thermal stability time. Samples with dimensions of 2 mm × 2 mm × 1 mm were placed into a tube with Congo red paper and put into an oil bath at 180°C. The time when Congo red paper began to turn to blue was defined as static thermal stability time.

Dynamic Thermogravimetric Analysis. Thermogravimetric analysis measurements were investigated by a TGA/DSC1/1100 SF thermal-analysis instrumentation (Mettler Toledo, Switzerland). PVC samples were carried out in a nitrogen atmosphere (50 cm³ min⁻¹) and heated from 50 to 650°C with the heating rates of 5, 10, 15, 20, and 25°C min⁻¹, respectively. The differential thermogravimetry (DTG) curves were also used in evaluating the thermooxidative stability of PVC and PVC containing 3 phr of the stabilizer. The temperature at the maximal rate of the weight loss (T_p), the mass loss for the first degradation step (Δm_1), and the mass loss for the second degradation step (Δm_2) were determined from DTG and TGA curves, respectively. The apparent activation energy (E) and preexponential factor (A) for the first degradation step were calculated according to the Kissinger method, where dehydrochlorination of PVC was the dominant reaction.²¹

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (1)$$

where T_p is the temperature at the maximal rate of the weight loss from the DTG curve, β is the heating rate, A is the preexponential factor, R is the gas constant, and E is the apparent activation energy.

RESULTS AND DISCUSSION

Characterization of ZnGly

Through element analysis and atomic absorption, the content of carbon, hydrogen, and zinc of the synthesized ZnGly are 21.89, 3.43, and 43.57%, respectively. The theoretical value of carbon, hydrogen, and zinc are 23.17, 3.86, 42.08%, respectively. The prepared ZnGly was well consistent with theoretical value. It could be concluded that such a method was suitable to obtain ZnGly.

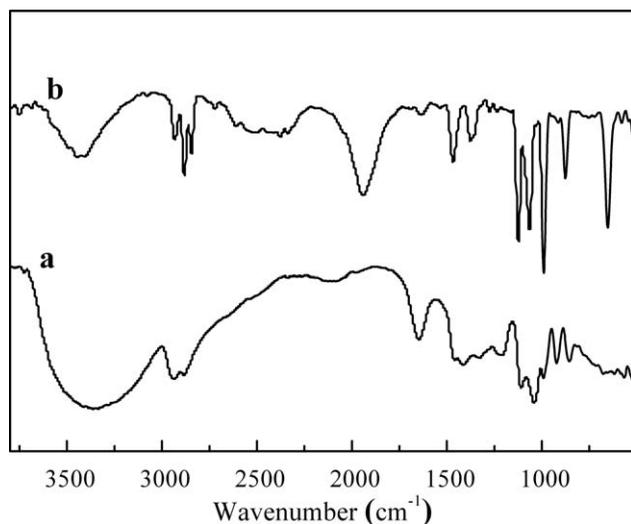


Figure 1. FT-IR spectra of glycerol (a) and ZnGly (b).

FT-IR spectra of glycerol (a) and the synthesized ZnGly (b) were shown in Figure 1. The bands at 3360, 2910, 1110, and 1040 cm^{-1} could be attributed to the characteristic $\nu(\text{O-H})$, $\nu(\text{C-H})$, and $\nu(\text{C-O})$ of glycerol. The narrowing of the glycerol bands in ZnGly was due to the crystalline nature of the material.²² The peaks at 3440, 2930, 1065, and 1241 cm^{-1} of ZnGly, were assigned to the characteristic $\nu(\text{O-H})$, $\nu(\text{C-H})$, and $\nu(\text{C-O})$. The band at 1467 cm^{-1} was due to the O-H bending mode. Compared with glycerol, a new band at 1940 cm^{-1} confirmed the formation of ZnGly phase and could be assigned to C-O stretching mode where the oxygen atom was involved in an O-H...O hydrogen bond.²³ Besides, the peak at 652 cm^{-1} , which was due to the Zn-O stretching mode, indicated the presence of Zn-O bond of sample.

For further identification of ZnGly, XRD patterns of the ZnO and the synthesized ZnGly were used as shown in Figure 2. The curves (a) and (b) represent ZnO and ZnGly, respectively. The XRD pattern of ZnGly showed that sharp and intense peaks at 10.9°, 11.3°, 17.2°, 20.7°, 23.8°, 24.7°, and 27.6°, indicating the

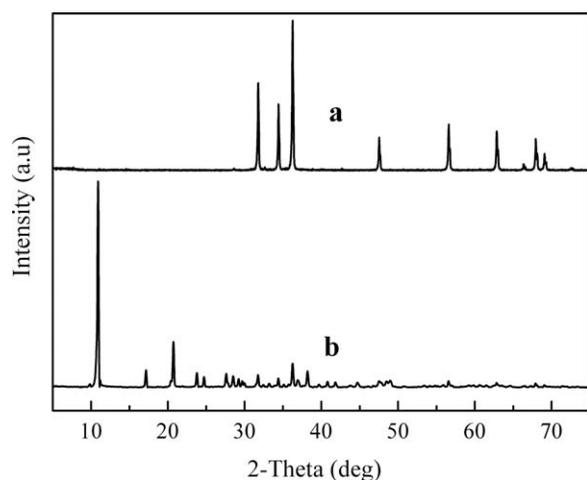


Figure 2. XRD patterns of ZnO (a) and ZnGly (b).

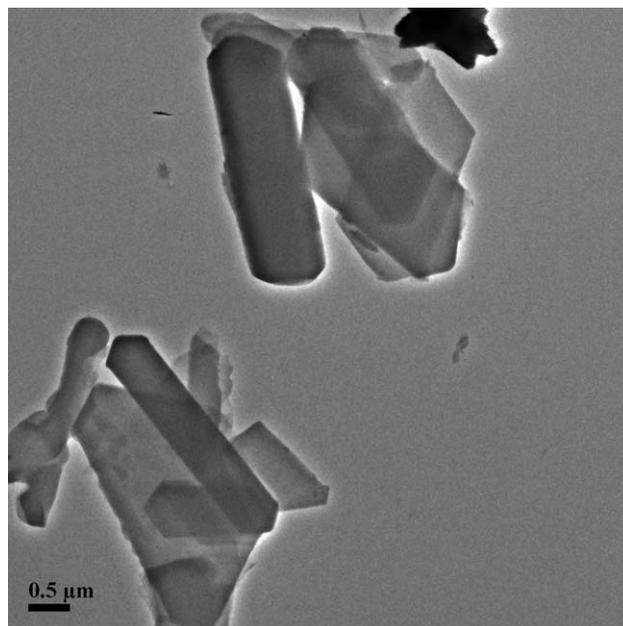


Figure 3. TEM images of ZnGly rods.

existence of well-crystallized ZnGly. The disappearance of the characteristic peaks in curve (a) also demonstrated the formation of ZnGly.

Figure 3 showed transmission electron microscopy (TEM) images of the ZnGly rods. Most of these products possessed rod-like structures with the length of 1.4–5.0 μm and diameter of 0.5–1 μm . The photos obtained from TEM can be also considered as a proof of well-crystallized ZnGly.

The typical TGA and its first-order differential (DTG) curves were shown in Figure 4. The TGA curve of ZnGly showed an obvious weight loss at the temperature of 408°C. The small weight loss of ZnGly at the temperature range of 25–330°C could be attributed to absorb water and other gases. The significant weight loss (~37.28%) at the temperature range from 330 to 500°C could be assigned to the removal of chemically

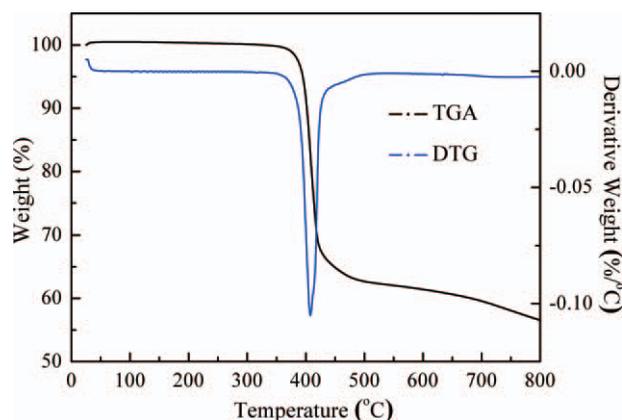


Figure 4. TGA and its corresponding DTG curves of ZnGly. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

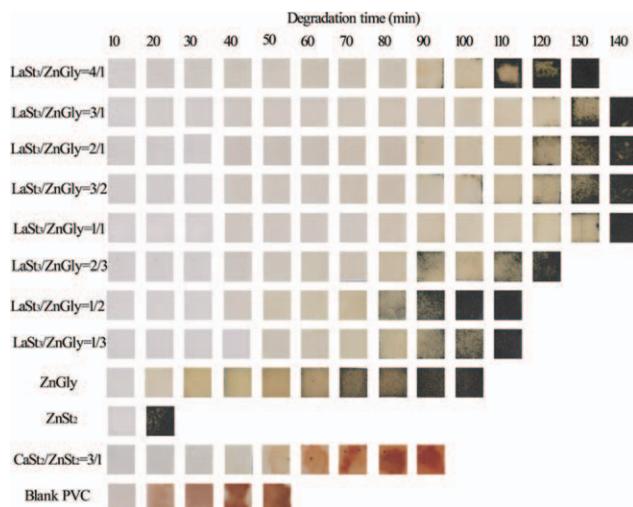


Figure 5. Color change of PVC strips with time at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bonded glycerol moiety. There was a total weight loss of 43.52% in the temperature range 25–800°C. The TGA results indicated that the ZnGly possessed high thermal stability, which was above about 330°C.

Thermal Stability of PVC Samples

The gradual change of color with time at 180°C for PVC strips containing 2 phr stabilizers was listed in Figure 5. The time needed for blackening the samples was measured as a criterion for the stabilizing efficiency. It was shown that the color of PVC strips containing ZnSt₂ alone became completely black after only 10 min and blank PVC strip turned red within 20 min. The PVC sheet containing ZnGly became pale yellow in 30 min and black after 80-min heating. Compared with ZnSt₂, a significant improvement was observed that ZnGly could delay the blackening time. It could be observed that the thermal stability of PVC strips were enhanced with increasing mass ratio of LaSt₃/ZnGly before 1/1 as shown in Figure 5. At optimized ratio of LaSt₃ and ZnGly, which meant LaSt₃/ZnGly equal to 1 according to Figure 5, the color of PVC strips maintained white during 80-min heating. Then the color became pale yellow at the time of 130 min which was higher than the sample stabilized by CaSt₂/ZnSt₂. It could be obtained that the initial color stability and long-term stability were markedly enhanced through combination of ZnGly with LaSt₃.

Table I showed the results of congo red test for the PVC containing 2 phr stabilizers as well as the influence of the mass ratio of LaSt₃/ZnGly on the thermal stability time of PVC. Moreover, ZnSt₂ and CaSt₂/ZnSt₂ were used as reference stabilizers to make a comparison. The results revealed that the investigated stabilizers displayed higher stabilization efficiency than the common stabilizer, as it was shown by the larger thermal stability time. The thermal stability time for the ZnGly was almost three times larger than the value for the ZnSt₂. Compared with ZnSt₂, ZnGly could inhibit dehydrochlorination of PVC greatly and lower its function on self-catalysis degradation process of PVC. There is a little difference in the thermal stability time for

Table I. Thermal Stability Time (T_s) of PVC Containing 2 phr of Stabilizers at 180°C

Code name	Thermal stability (T_s) (min)
LaSt ₃ /ZnGly = 1/0	15.3
LaSt ₃ /ZnGly = 3/1	22.6
LaSt ₃ /ZnGly = 2/1	22.3
LaSt ₃ /ZnGly = 3/2	22.1
LaSt ₃ /ZnGly = 1/1	22.5
LaSt ₃ /ZnGly = 2/3	22.6
LaSt ₃ /ZnGly = 1/2	22.7
LaSt ₃ /ZnGly = 1/3	22.5
LaSt ₃ /ZnGly = 0/1	21.7
CaSt ₂ /ZnSt ₂ = 3/1	17.8
ZnSt ₂	7.4
Blank PVC	5.8

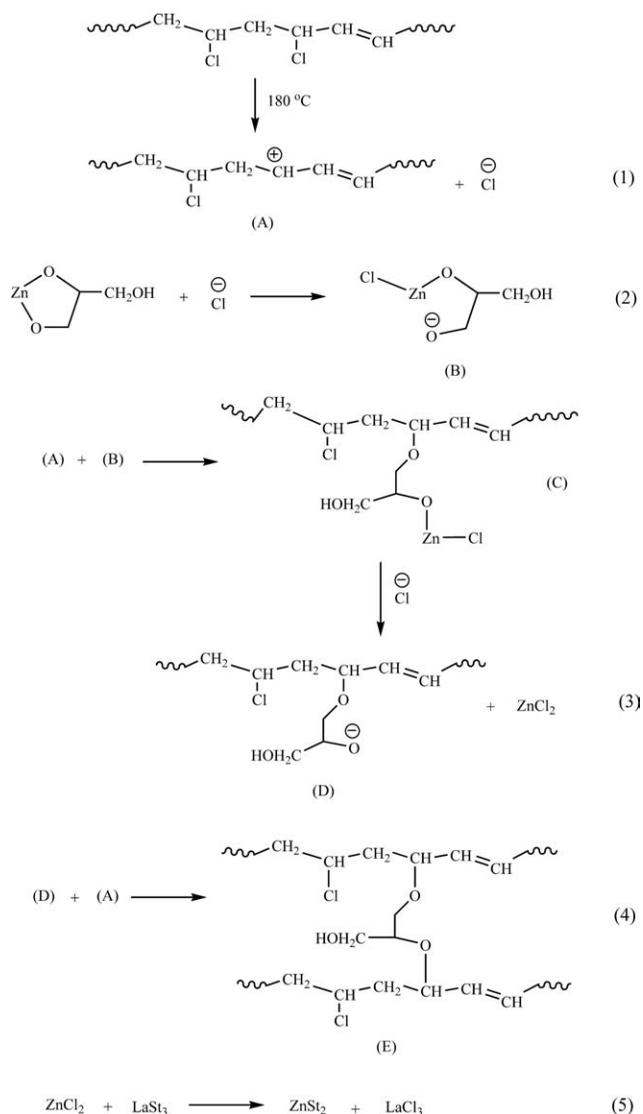


Figure 6. A possible mechanism for the stabilizing efficiency of LaSt₃/ZnGly.

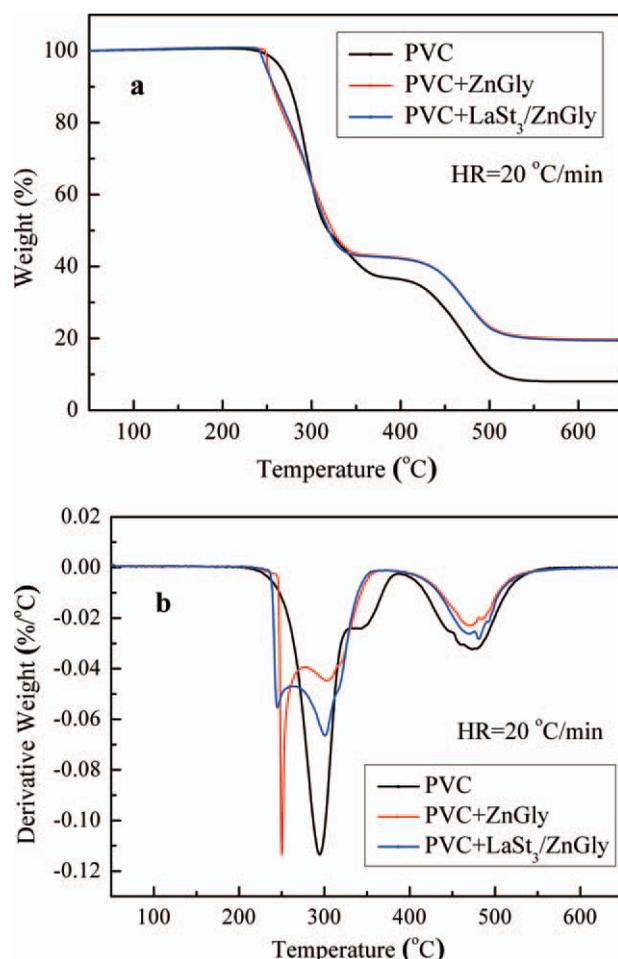


Figure 7. TG and DTG curves for nonstabilized and stabilized PVC at the heating rate of $20^{\circ}\text{C min}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the mass ratio of $\text{LaSt}_3/\text{ZnGly}$ between 1/3 and 3/1 that is larger than the thermal stability time for PVC containing $\text{CaSt}_2/\text{ZnSt}_2$ with the mass ratio of 3/1 and LaSt_3 alone according to our experiments. Therefore, the ZnGly is a promising stabilizer which can be used in PVC because of its excellent initial color stability and better efficiency of stability. Also, LaSt_3 could be added as costabilizer to improve the thermal efficiency of PVC.

To investigate a possible mechanism which could explain the stabilizing efficiency of ZnGly , experiments were carried out to investigate the mode of action of ZnGly as the thermal stabilizer for PVC.²⁴ ZnGly was subjected to the stream of dry HCl gas, at 180°C , in air for 30 min. Then the product was dried at 120°C for 3 h to eliminate the residual HCl . The deionized water was added into the processed product, dissolving for a certain time and filtering. Silver nitrate solution (0.5%) and atomic absorption showed that the chloride ions and zinc ions were present in the filtrate, respectively. This confirmed ZnGly could act as an HCl absorber, and further indicated that ZnCl_2 was generated.

A possible mechanism for the stabilizing efficiency of ZnGly during the thermal degradation of PVC was shown in Figure 6. A newly generated chlorine atom from the defective PVC chain was absorbed by ZnGly (Reactions 1 and 2). The structure (B) could react with the changed PVC chain (A) (Reaction 3). The subsequent stage could be to combine the obtained structure (D) and structure (A) into the much more stable structure (E) (Reaction 4). The ZnCl_2 , which was generated in Reaction 3, could react with LaSt_3 . The reaction could produce another effective thermal stabilizer ZnSt_2 (Reaction 5). From the aforementioned reactions, one could explain the highly synergistic effect of $\text{LaSt}_3/\text{ZnGly}$.

Dynamic Thermogravimetric Analysis

The result obtained from the dynamic thermogravimetric analysis of blank PVC and PVC containing 3 phr thermal stabilizers

Table II. The Characteristics of the Dynamic Thermogravimetric Degradation Analysis Curves and Kinetic Parameters of the Degradation of the Investigated Samples

Components	Heating rate ($^{\circ}\text{C min}^{-1}$)	T_p ($^{\circ}\text{C}$)	Δm_1 (%)	Δm_2 (%)	Δm (%)	E (kJ mol^{-1})	$\ln A$	$E/\ln A$
PVC	5	269.63	65.35	29.49	95.11	139.76	29.66	4.71
	10	281.61	64.57	29.11	93.66			
	15	290.30	64.55	29.14	93.46			
	20	295.00	63.76	28.80	92.41			
	25	299.01	65.21	29.07	94.20			
PVC+ZnGly	5	222.41	57.89	29.49	80.84	110.45	25.51	4.33
	10	234.33	58.35	22.68	80.86			
	15	241.93	57.83	23.06	80.84			
	20	246.69	58.01	22.60	80.90			
	25	251.61	58.42	23.52	82.14			
PVC+ $\text{LaSt}_3/\text{ZnGly}$	5	237.84	59.31	22.43	82.88	42.54	7.82	5.44
	10	252.16	58.57	22.93	81.44			
	15	291.08	58.02	22.97	81.04			
	20	298.14	58.31	22.98	80.69			
	25	301.47	58.47	22.57	81.12			

at the temperature interval 50–650°C was shown in Figure 7. Stabilizers were ZnGly and LaSt₃/ZnGly (1/1), respectively. It could be found that there were two thermal degradation steps of all investigated samples. The first degradation step can be attributed to dehydrochlorination and the following step is related to cyclization of polyenes, crosslinking, and benzene formation.²⁵ It was also shown in Figure 7(a) that the existence of ZnGly and LaSt₃/ZnGly decreased the weight loss of the first and second degradation steps.

The apparent activation energy (E) and the preexponential factor (A) were calculated and listed in Table II. According to compensation ratio $E/\ln A$, the greater ratio value means the greater stability of the system.²⁶ Table II showed that the value of $E/\ln A$ for blank PVC was greater than PVC containing ZnGly. This behavior could be explained by the catalysis effect of ZnCl₂ generated during heating of sample. Nevertheless, the value of $E/\ln A$ for blank PVC was less than PVC containing LaSt₃/ZnGly. This indicated that combination of LaSt₃ with ZnGly presented an obvious improvement of stability on thermal degradation of PVC.

CONCLUSIONS

ZnGly was prepared by treating ZnO with glycerol. The TEM images showed that ZnGly possessed a rod-like structure with a length of 1.4–5.0 μm and diameter of 0.5–1 μm. ZnGly was proven to be an efficient thermal stabilizer for PVC. Compared with ZnSt₂, it was demonstrated that initial color stability was markedly improved and the thermal stability time was obviously extended through adding ZnGly. In comparison with CaSt₂/ZnSt₂, the combination of LaSt₃ and ZnGly in investigated proportions greatly improved the extent of discoloration and also increased the thermal stability time. The color of PVC sample containing LaSt₃/ZnGly in mass ratio of 1 maintained white during 80-min heating and became pale yellow at the time of 130 min, which was higher than the sample stabilized by CaSt₂/ZnSt₂. Static oven test and congo red test verified that the better percent of ZnGly in the LaSt₃/ZnGly should be 50%. The dynamic analysis of thermogravimetric confirmed that combination of LaSt₃ with ZnGly presented an obvious improvement of stability on thermooxidative degradation of PVC. Herein, the ZnGly was a promising stabilizer which could be used in PVC because of its excellent initial color stability and better efficiency of stability. Also, LaSt₃ could be added as costabilizer to improve the thermal efficiency of PVC.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from the National “Twelfth Five-Year” plan for Science & Technology (2012BAD32B03), the Cooperative Innovation Foundation of Industry, Academy and Research Institutes (No. BY2010118) in Jiangsu Province of China.

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