

The Effect of Pentaerythritol-Aluminum on the Thermal Stability of Rigid Poly(vinyl chloride)

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ABSTRACT: Pentaerythritol-aluminum (PE-Al) was synthesized by a solid-phase reaction in this study. The formation and characteristics of PE-Al were confirmed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). SEM images showed that the shapes of PE-Al particles were spherical and the average size was around 23 nm. The thermal properties of rigid poly(vinyl chloride) (PVC) with PE-Al were tested by Congo red test, thermal aging test, conductivity test, thermogravimetric analysis (TGA), and UV-visible spectroscopy test. The results showed that combination of PE-Al, in comparison with commercial thermal stabilizers, presented an obvious improvement in stabilization efficiency of PVC. Moreover, addition of PE-Al could significantly prolong static stability time of PVC, reduce weight loss, and improve the initial color of PVC films. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3704–3709, 2013

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INTRODUCTION

As is known, poly(vinyl chloride) (PVC) is one of the most important commercial polymers in the world.¹ Its products are widely used in paints, coatings, films, medical devices, and food packaging.² However, PVC will release hydrogen chloride (HCl) when temperature reaches 100°C and above because of the drawbacks in its structure, resulting in the degradation of polymer backbone and deterioration of the polymer properties.³ Therefore, appropriate stabilizers must be added to restrain the degradation.⁴

Generally speaking, stabilizers can restrain the thermal degradation of PVC in the following manner:

- Replace the labile chlorine atoms (e.g., allylic or tertiary chlorine atoms) in PVC chains to prevent the formation of conjugated double bonds.^{5,6}
- Absorb HCl released during the degradation of PVC to diminish its self-catalytic growth. Such stabilizers cannot protect PVC against short time discoloration but they delay catastrophic degradation of the material.^{5,6}

The stabilizers currently used include lead salts, metallic soap salts (CaSt₂/ZnSt₂), organic tin, and rare earth stabilizers.⁷ Lead salt stabilizers are the most useful and efficient thermal stabil-

izers. Their applications, however, are inhibited on account of their high toxicity.^{8,9} Other kinds of commercially available PVC thermal stabilizers are Ca/Zn stabilizers. Low toxicity stabilizers, they are widely used in food packaging materials, children's toys, and bottle seals.¹⁰ However, because of their marked "zinc burning" effect, Ca/Zn stabilizers have some defects in long-term stability.¹¹ Rare earth is also an important stabilizer that has higher stabilizing efficiency on rigid PVC because of its longer incubation period and lower rate of degradation in comparison with Ca/Zn stabilizer.^{12,13} However, their poor early (initial) stabilization effect limits their application as PVC stabilizers.⁴

Pros and cons of commercial heat stabilizers considered, the preparation of new stabilizers must be put on the agenda. Recently, pentaerythritol has been widely investigated as an important costabilizer¹⁴; Al 4180,¹⁵ produced by Farstab Stabilizer Company, is a representative commercial heat stabilizer which is a complex mixture containing Al (III). James L. Dever and Degang Li^{16,17} had reported the synthesis of pentaerythritol-zinc and studied its static and dynamic thermal stability. Li's study showed noticeable improvement in PVC thermal stability as result of it. It is known that the valence electron structure of Aluminum is 3s²3p¹ while Zinc is 4s²4p¹, and their physical and chemical properties are similar to a limited

Table I. Pre-mix: Rigid PVC- Each Stability Agent Formulation

Thermal stabilizers		Stability agent formulation (wt %)			
Ca/Zn	CaSt ₂ : 20	ZnSt ₂ : 30	Dibenzoylmethane: 10	Phosphite ester: 15	Other additives: 25
Lead salts	Tribasic lead sulfate: 40	Dibasic lead phosphite: 20	Polyethylene wax: 20	Assistant agent: 20	
PE/Al ₂ O ₃	PE: 86	Al ₂ O ₃ : 14			
PE-Al	PE-Al: 100				

PE, pentaerythritol; PE-Al, pentaerythritol-aluminum.

extent. For example, AlCl₃ and ZnCl₂ are both Lewis acid. Therefore, pentaerythritol-aluminum (PE-Al) may have similar properties.

In this article, PE-Al was prepared from pentaerythritol and Al₂O₃ through a solid-phase reaction. The formation and characteristics of PE-Al were analyzed by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). SEM images showed that PE-Al particle was uniform and the shape was quite regular. Its thermal stability for rigid PVC was also studied. The results showed that the best amount of PE-Al when used as single thermal stabilizer was 3.84 phr. Moreover, PVC with PE-Al exhibits excellent long-term thermal stability and initial color. The catalytic effect of the Al-based thermal stabilizers on the decomposition of PVC was not observed when PE-Al was used.

EXPERIMENTAL

Materials

PVC resin and thermal stabilizers, for example, CaSt₂/ZnSt₂ stabilizers and lead salt stabilizers were kindly supplied by Huike Additives Company, China. Ca/Zn stabilizers consisted of calcium stearate (20 wt %), zinc stearate (30 wt %), β-diketone, and other additives. The lead salts stabilizer was composed of tribasic lead sulfate, dibasic lead phosphite, polyethylene wax, and assistant agent. The stability agent formulations are shown in Table I. Pentaerythritol, Al₂O₃, and other chemical agents are all AR grade.

Preparation of PE-Al

About 0.45 mol pentaerythritol (PE) and 0.1 mol Al₂O₃ were put into a high-speed mixer set at 3000 r/min for 5 min. Then the homogeneous powder was put into an oven with a motor stirring under 200 ± 1°C for 2 h.

Preparation of PVC Samples

All experiments were performed with a standardized pre-mix (so-called “naked” pipe-formulation) which included PVC (powder, 100 phr), CPE (powder, 9 phr), ACR (powder, 2 phr), TiO₂ (powder, 4 phr), CaCO₃ (powder 20 phr), and stearic acid (powder, 1.6 phr) (Table II). Sixty gram pre-mix and 1.76 g heat stabilizers were mixed in a high-speed mixer. Subsequently, the mixture was milled by an open two-roll at 180°C for 5 min. The drawn-out sheets were 1.0 ± 0.1 mm thick.

Test Methods

Scanning Electron Microscopy. The morphology of PE-Al powder was determined by using SEM. Sputtering technique was

used to coat the samples. The samples were observed by Sirion 200, the Netherlands.

Fourier Transform Infrared (FTIR) Spectroscopy. The functional groups of PE-Al were analyzed by FTIR (Nicolet-560FTIR). KBr-supported test samples were used in the spectra range of 4000–400 cm⁻¹ with 120 scans at a resolution of 4 cm⁻¹.

Thermal Stability of PE-Al

Congo Red Test Method. According to ASTM D4202, 2 g PVC samples were cut into 0.2 mm squares before being put into a test tube with Congo red test paper located 1.5 cm above the sample. The tube was heated in an oil bath for evaluation of the static thermal stability of samples. The temperature was 180°C. The time when Congo red test paper begins to turn to blue was defined as static stability time (*T_s*).

Thermal-Aging Test. The PVC film was cut into 1 cm², which were subsequently subjected to static thermal aging by being heated in an electrothermal constant-temperature dry box at 180°C in air. The samples were removed every 10 min.

Conductivity Test. The amount of HCl released from PVC samples was measured on a conductivity meter.^{5,9} 0.50 g PVC samples were cut into 2.0 mm² and placed in the reaction vessel. Nitrogen gas (7.0 L/h) was then used to transport HCl released by the degradation of PVC samples. The test temperature was 180°C. Conductivity of the solution in the measuring vessel was measured by conductimeter. The induction time spans the period between the start of heating and the point when the conductivity of solution starts to increase, and the

Table II. Pre-mix: Rigid PVC Formation

Pre-mix: Rigid PVC formation	Parts per hundred resin (phr ^a)
PVC	100.0
Chlorinated polyethylene (CPE)	9.0
Acrylic copolymer (ACR)	2.0
TiO ₂	4.0
CaCO ₃	20.0
Stearic acid (HSt)	1.6

PVC, poly(vinyl chloride).

^aphr, parts per hundred parts of resin.

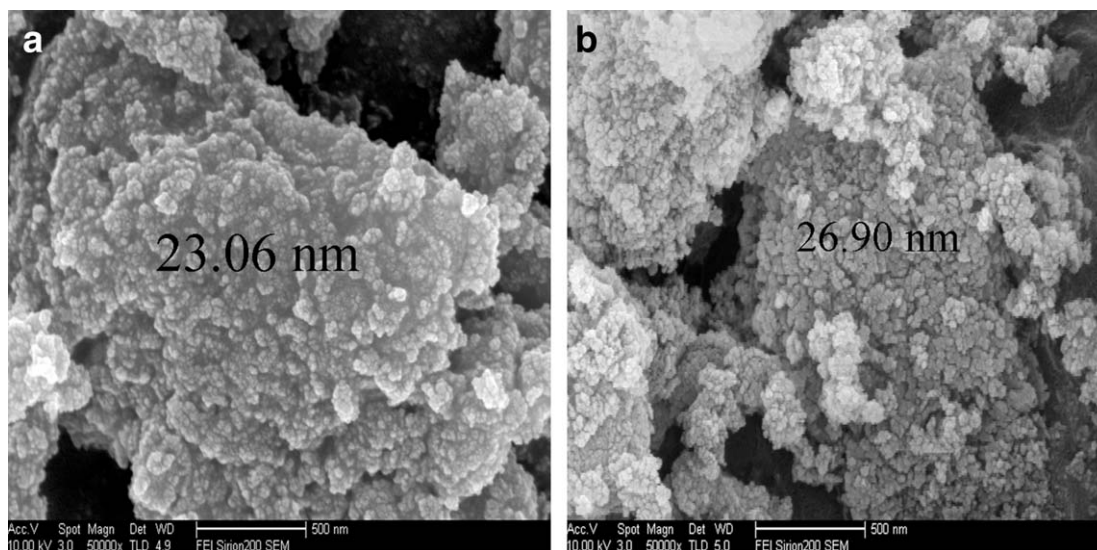


Figure 1. (a) SEM image of PE-Al. (b) SEM image of Al_2O_3 .

period hereafter until the conductimeter reading reaches $50 \mu\text{s}/\text{cm}$ is stability time.

Thermogravimetric Analysis. Thermal degradation studies were conducted on a thermogravimetric analyzer. All the samples were evaluated from 25°C to 600°C and the weights were taken in the range of 20–25 mg. Argon atmosphere was used in both kinds of test and the heating rate was $10^\circ\text{C}/\text{min}$.

UV-Visible Spectroscopy Test. The optical spectra of the PVC samples with different components were recorded on a UV-2450PC UV-visible spectrometer with slit width set at 2 nm over the wavelength in the range of 200–500 nm. The samples were placed in an oven at 180°C for 120 min. The temperature of UV-visible experiment was kept at room temperature (25°C) and freshly distilled peroxide-free tetrahydrofuran (THF) was used as solvent.

RESULTS AND DISCUSSION

The Structure of PE-Al

Scanning Electron Microscope. SEM is used to inspect the size of the powder. Figure 1(a) shows the SEM image of solid-phase synthesized PE-Al. It can be seen from Figure 1(a) that the nanoparticles are agglomerated in the form of clouds (with average diameter of 23 nm). This agglomeration may be a result of van der Waals forces or hydrogen bonding¹⁸ between individual particles. Because the PE-Al is prepared by solid-phase reaction technique, the reaction may not reach the end point. Unreacted $-\text{OH}$, therefore, may be in the structure and can form hydrogen bonding easily. Figure 1(b) displays the SEM micrograph of nanometer Al_2O_3 , the particles of which have an average size of 26.90 nm while that of PE-Al is 23 nm. Comparison of the two micrographs shows that the size of PE-Al particle is uniform and the shape is quite regular.

Fourier Transform Infrared. FTIR analysis is used to prove the characteristics of functional groups of PE-Al. Pure PE and PE-Al are prepared for the test. The spectra show that the sharp

peak (3327 cm^{-1}) of the $-\text{OH}$ stretching vibration band in the pure PE becomes broad in PE-Al. The weak peak at 1636 cm^{-1} comes from vibration absorption peak of water and 1453 cm^{-1} represents the longitudinal phonon vibration peak of Al_2O_3 .¹⁹ The multiple peaks between 1000 and 1400 cm^{-1} imply the existence of C–O in polyols. In addition, the wavenumber of the $-\text{OH}$ band shifts from 3327 to 3447 cm^{-1} (as shown in Figure 2) and the characteristic peak of PE (878 and 664 cm^{-1})¹⁴ disappears in the PE-Al compound. The results indicate that the interaction between PE and Al_2O_3 can destroy the intermolecular force or intramolecular force of the materials to make a shift of the peaks. In general, alcohols are weak base. The acidity of polyhydric alcohols is higher than that of the normal alcohol. For example, the pK_a of glycerol is 14.1. Therefore, just as the reaction of glycerol and ZnO can form $\text{CH}_2\text{O}-\text{Zn}$ type bonds, during which water is generated, so PE can react with Al_2O_3 to produce PE-Al and H_2O .²⁰

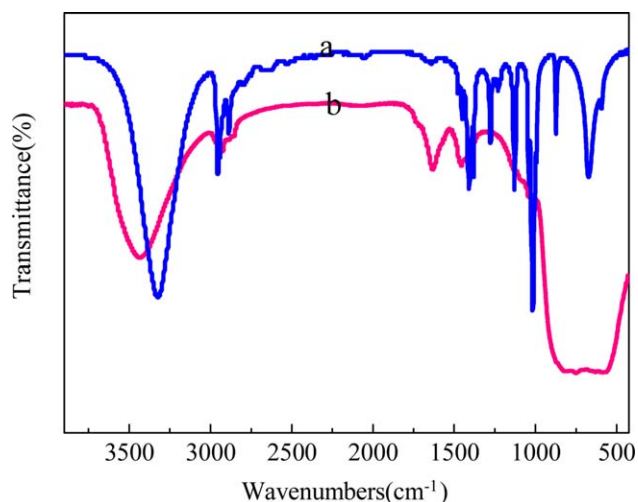


Figure 2. FTIR spectra of (a) PE and (b) PE-Al. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

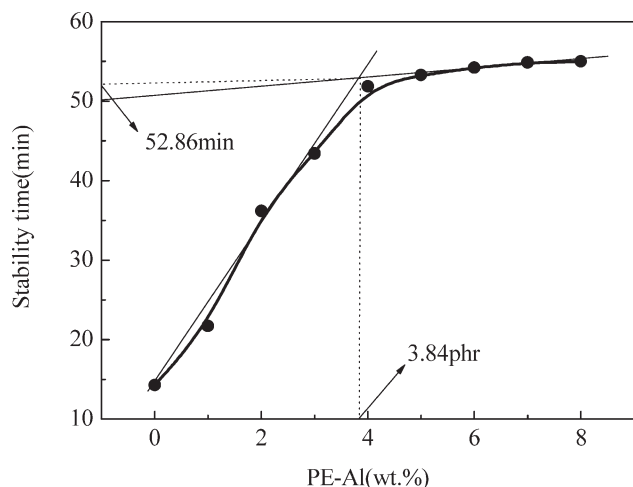


Figure 3. Different amount of PE-Al on the stability time of PVC (pre-mix).

Thermal Stability of PE-Al

Starting Effect Content of Stabilizers Analysis. It is commonly known that selecting suitable quantity of heat stabilizers is very important. In order to confirm the most appropriate contents of PE-Al, different amount of PE-Al is added into pre-mix for PVC stability testing. The stability time of the system is obtained by Congo red test method. As shown in Figure 3, the results indicate that PE-Al greatly extends the thermal stability time (T_s). In the absence of PE-Al, it takes a short heating time (about 15 min) before the indicator paper changes color. With addition of PE-Al, T_s increases, proportional to that in PE-Al. However, as T_s of PVC reaches 54.91 min with PE-Al increasing to 8 phr, it stops going up with increase of the latter. Intersection of the two extrapolations shows that the optimum amount of PE-Al is 3.84 phr and T_s 52.86 min in this condition.

Compared with pure PVC, the stability time of PVC with PE-Al is significantly extended. There are two possible reasons. One is that the interaction between PE-Al and the labile chlorine atom of PVC chains makes the dehydrochlorination difficult to continue because the electronegativity of allyl chlorine (about 3.16) in PVC chains is high, which makes its reaction with the low-electronegativity aluminum atom (about 1.61) in PE-Al easy. The other is that PE-Al acts as an HCl scavenger and therefore suppresses autocatalytic degradation because the electronegativity of hydrogen atom on HCl is very low (about 2.20) while that of the oxygen atoms (about 3.44) in PE-Al is high, making electrophilic reaction thereof easy.²¹

Comparison of Several Heat Stabilizers. As shown in Figure 4, the T_s of all the thermal stabilizers are enhanced compared with pure PVC (pre-mix). The T_s of pure PVC (pre-mix) is only 15 min while that of PVC with lead salts are 58 min with higher efficiency in retarding the release of HCl from PVC at 180°C. The T_s of PVC with Ca/Zn is 30 min, which means relatively low thermal stability against degradation of PVC. Compared with the commercial thermal stabilizers, the T_s of PVC with PE-Al and PE/Al₂O₃ are 50 and 28 min, respectively. The data show that T_s of PVC with PE-Al is similar to that of PVC with

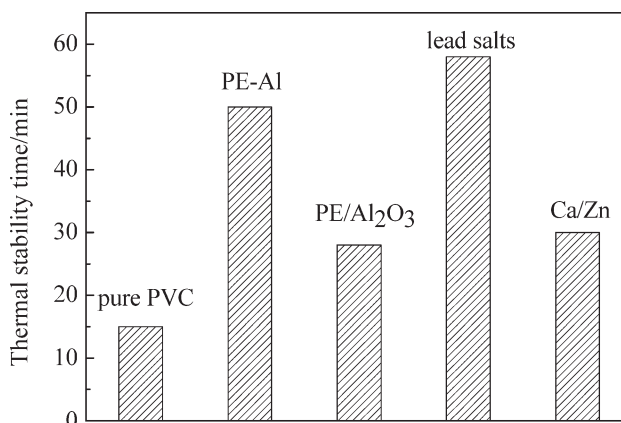


Figure 4. Comparison of the thermal stability time by different thermal stabilizers.

lead salts, which suggests the efficiency of PE-Al on stabilization of PVC.

In order to prove the amount of HCl evolution from PVC films, conductivity test was used (Figure 5). From the curves, it is observed that the amount of HCl evolution from PVC films without thermal stabilizers starts to increase after a short induction time (15.11 min) while the films with stabilizers show longer induction time, which are 21.05, 22.42, 41.86, and 33.71 min, corresponding to PE/Al₂O₃, CaSt₂/ZnSt₂, lead salts and PE-Al system, respectively. The data show that upon addition of heat stabilizers the induction time changes significantly. Concomitantly, the stability time is extended and the stability time of PVC with PE-Al is longer than that with lead salts.

Discoloration Test

It is well known that thermal degradation of PVC happens along with the color change when the sheets are heated. The effect on the thermal stability of materials is studied by discoloration tests to monitor the degradation degree. Some fine but

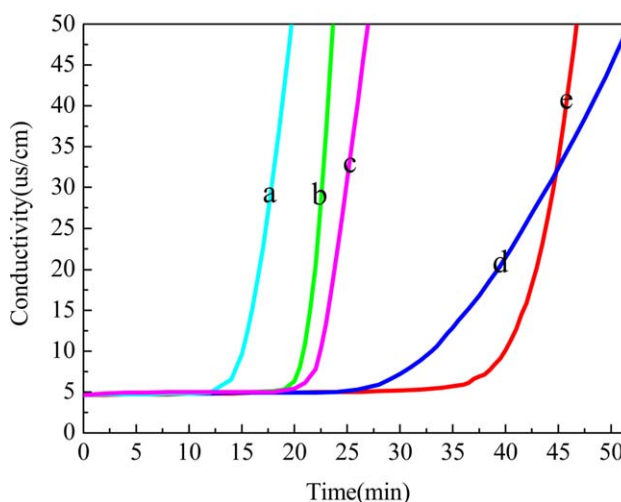


Figure 5. Change of conductivity of aqueous solution with respect to time at 180°C for PVC with and without stabilizers: (a) pure PVC; (b) PE/Al₂O₃; (c) CaSt₂/ZnSt₂; (d) PE-Al; and (e) lead salts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Color Evolutions, as a Function of Time, of PVC Samples Heated at 180°C
[Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Stabilizers	Degradation time, ×10 min											
	0	2	4	6	8	10	12	14	16	18	20	
Pure PVC												
Lead salts												
CaSt ₂ /ZnSt ₂												
PE-Al												
PE/Al ₂ O ₃												

PE, pentaerythritol; PE-Al, pentaerythritol-aluminum; PVC, poly(vinyl chloride).

perceptible differences in color of PVC with and without heat stabilizers are observed (Table III) and the test temperature is 180°C. Results show that pure PVC begins to color at the mixing stage and becomes completely black after being heated at 180°C for merely 20 min. The color of the PVC samples containing PE/Al₂O₃ turns brown and then becomes completely black after 40 min. As one of the most popular commercial PVC stabilizers, the stability of CaSt₂/ZnSt₂ system is still negative and when the samples with CaSt₂/ZnSt₂ are heated for 40 min, the sheets start to color. As for lead salts which are among the most effective heat stabilizers, the thermal stability is commendable. Meanwhile, the stability of PE-Al is somewhat on the inferior side with lead salts. Table III also shows that PVC strips exhibit excellent initial color with addition of PE-Al.

Thermogravimetric Analysis

The TGA tests for the pure PVC with different heat stabilizers are shown in Figure 6. All the experiments are conducted from

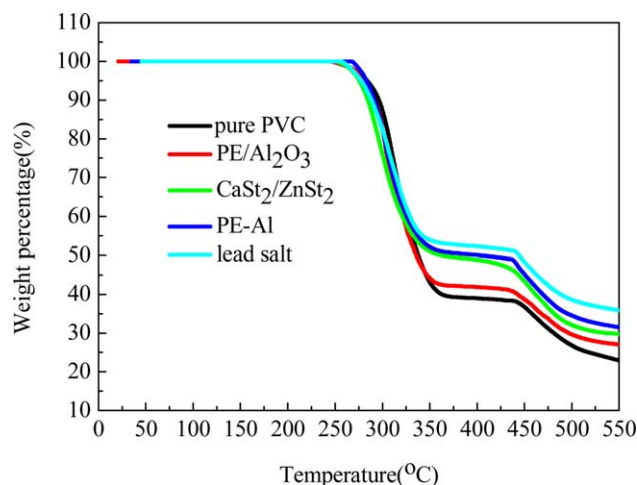


Figure 6. TGA results for PVC with and without stabilizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

room temperature to 600°C, and the sample weights are taken in the range of 20–25 mg. As shown in all the five curves, it is obvious that the thermal degradation consists of two steps. The first step sees HCl releasing from PVC chains and subsequent

Table IV. Weight Loss of PVC Samples Stabilized with and Without Heat Stabilizers

Formation	After the first-step (%)	After the second-step (%)
Pure PVC	60.67	77.32
PE/Al ₂ O ₃	57.57	73.18
CaSt ₂ /ZnSt ₂	49.98	70.50
PE-Al	48.93	68.69
Lead salts	46.49	64.35

PE-Al, pentaerythritol-aluminum; PVC, poly(vinyl chloride).

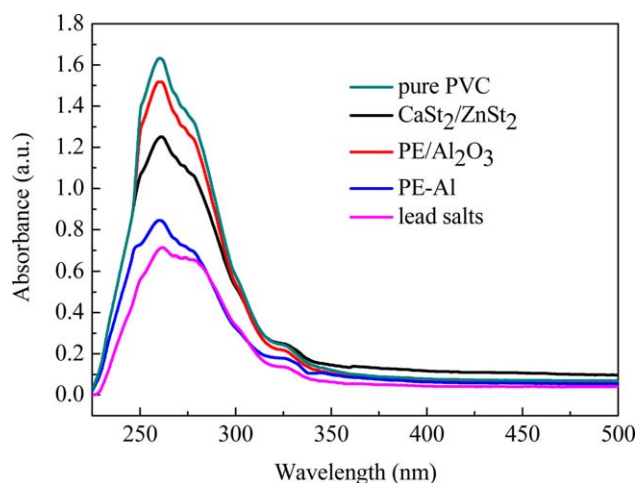


Figure 7. UV spectra of the pure PVC stabilized with and without heat stabilizers and treated for 120 min at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of conjugated polyenes; the second step involves scission of polyene sequences to low-molecular-weight hydrocarbons with linear or cyclic structure.^{4,22} In addition, it can be seen from the curves that the onset degradation temperature (T_d) for PVC with PE/Al₂O₃, lead salts, and CaSt₂/ZnSt₂ are identical (about 249°C) while the T_d for PVC with PE-Al is 266°C. Table IV shows weight loss (100% weight percentage) for PVC with different heat stabilizers. It shows that weight loss becomes increasingly obvious with the rise in temperature. It is noted that the weight loss of pure PVC (60.67%) is obvious at the first stage of thermal decomposition while this phenomenon disappears with addition of heat stabilizers. A comparison between Figure 6 and Table IV reveals that the addition of lead salt causes an obvious reduction in weight loss, which drops to 46.49%, the lowest of all PE-Al comes second with 48.93% weight loss at the same thermal decomposition time.

UV-Visible Spectroscopy Test

Figure 7 shows the UV-visible spectra of PVC with different heat stabilizers aged at 180°C for 120 min. By studying the absorption intensity of the samples and the position of the absorption peaks, it is impossible to conclude the length and concentration of the conjugated double bonds which originated from the degradation of the PVC.^{23,24} Figure 7 shows that absorbance of pure PVC, PE/Al₂O₃, CaSt₂/ZnSt₂, PE-Al, and lead salts system is 1.63, 1.51, 1.25, 0.85, and 0.72, respectively. It indicates that the concentration of the conjugated bonds of PVC filled with PE-Al and lead salts system is smaller than that of the PVC samples filled with the other heat stabilizers. It shows that PE-Al can improve the thermal stability of the PVC resin.

CONCLUSION

PE-Al was successfully prepared by solid-state reaction using pentaerythritol and Al₂O₃ in a molar ratio of 4.5:1. The formation and characteristics of PE-Al was analyzed by SEM and FTIR. SEM images showed that PE-Al particles were regular. FTIR data showed that the interaction between PE and Al₂O₃ can destroy the intermolecular force or intramolecular force of the materials. The thermal stability test showed that PE-Al can prolong the degradation of PVC, improve color stability, and reduce the weight loss because of the replacement of the labile chlorine atoms in PVC chains. The results showed that the best amount of PE-Al used as single thermal stabilizer is about 3.84 phr and T_s was 52.86 min in this condition. Moreover, UV-visible spectroscopy showed that PE-Al can reduce the concentrations of the conjugated double bonds. To sum up, PE-Al was an excellent thermal stabilizer for rigid PVC.

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