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Design and synthesis of a new mannitol stearate ester-based aluminum alkoxides as a novel tri-functional additive for poly(vinyl chloride) and its synergistic effect with zinc stearate

Wenyuan Han[a], Manqi Zhang[a], Degang Li[a,]*, Tianbao Dong[a],

Bing Ai[a], Jianping Dou[c], Hongqi Sun[b,]*

[a]School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000, P. R. China

[b]School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, WA 6027, Australia

[c]Zibo Environmental Monitoring Station, Zibo 255000, P. R. China

ABSTRACT

The thermal stabilizers, lubricant, and plasticizers are three crucial additives for processing poly (vinyl chloride) (PVC). In this study, a new mannitol stearate ester-based aluminum alkoxides (MSE-Al) was designed and synthesized as a novel additive for PVC. The thermal stability and processing performance of PVC stabilized by MSE-Al were evaluated by Congo red test, conductivity measurement, thermal aging test, ultravioletevisible (UV-vis) spectroscopy test, and torque rheometer test. Results showed that the addition of MSE-Al can not only markedly improve the long-term thermal stability of PVC, but also greatly accelerate the plasticizing and decrease the balance torque which demonstrated that MSE-Al possesses the lubricating property. Thus, MSE-Al was demonstrated to be able to provide tri-functional additive roles, e.g., thermal stabilizer, plasticizer, and lubricant. The test results for the thermal stability of PVC indicated that the initial whiteness of PVC stabilized with MSE-Al was not good enough, thus the synergistic effect of MSE-Al with zinc stearates ($ZnSt_2$) on the thermal stability of PVC was also investigated. The results showed that there exhibited an appreciable synergistic effect between MSE-Al and $ZnSt_2$. The thermal stabilization mechanism and synergism effect of MSE-Al with $ZnSt_2$ were then discussed.

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* Corresponding author Tel: +86 18766957507 E-mail address: ldg@sdut.edu.cn (Degang Li); E-mail address: h.sun@ecu.edu.au (Hongqi Sun)

Keywords: Poly(vinyl chloride); tri-functional additive; mannitol stearate ester-based aluminum alkoxides; synergistic effect

1. Introduction

Poly(vinyl chloride) (PVC) is formed by the polymerization of vinyl chloride monomer. PVC has many attractive characteristics, for example, corrosion resistance, wear resistance, flame retardancy and insulation, and therefore has been widely used in industries, agriculture, construction, and electric power. PVC has become one of the most widely used plastics in the world because of its outstanding properties [1-3]. Due to the defects in the chain structure, there are a small amount of unstable chlorine in PVC. When PVC is exposed to heat, ultraviolet radiation, etc., unstable chlorine atoms will release in the form of hydrogen chloride. Unsaturated C-C bonds will appear in the molecular chains of PVC. The Unsaturated C-C bonds will lead to newly emerged unstable chlorine atoms, for instance, allyl chloride. Thermal degradation would normally occur when PVC is heated at above 100 ºC, while the processing temperature of PVC is 180 ºC. Thus, thermal stabilizers must be added to improve the thermal stability of PVC during processing. Furthermore, being a strong Lewis acid, hydrogen chloride produced from the degradation of PVC catalyzes the further degradation of PVC. This leads to the formation of a "zipper" dehydrochlorination reaction, resulting in a change in the color of the PVC (from white to brown, and to black at last), which further changes the properties of the PVC [4, 5].

In general, PVC thermal stabilizers should have at least two functions: (1) replacing or passivating labile chlorine atoms in the PVC chain, such as allyl chloride atoms, preventing the formation of conjugated double bonds; (2) absorbing or neutralizing HCl produced during the degradation of PVC to inhibit the autocatalytic dehydrochlorination reaction [6-8]. At present, common thermal stabilizers of PVC include lead salts [9], organotin [6], rare earth [10], calcium and zinc soap salts (especially the calcium and zinc stearates) [11]. The lead salts have an excellent long-term thermal stability, simple production process and low price. However, due to the toxicity on humans and the environment, their use has been restricted. The organotin thermal stabilizers are effective, but they are often used in high-grade PVC products because of the complex production processes and high production costs, which reduce their competitiveness with other thermal stabilizers. Moreover, certain organotins based on mercaptides also generate unpleasant odors [6]. The rare earth thermal stabilizers are similar to organotin, but expensive than the others, and the cost hinders the widespread application of rare earth thermal stabilizers. Ca/Zn metallic salts are non-toxic, environmentally friendly thermal stabilizers. Calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$) stabilizer contains fatty acid root, which makes these thermal stabilizers have good lubrication properties and relatively easy to be processed [12, 13]. Moreover, $ZnSt_2$ has an ability to replace the active allyl chloride and then significantly increase the initial color of PVC. Thus PVC products with calcium-zinc thermal stabilizers have a good initial color and smooth surface characteristics. However, the reaction between $ZnSt_2$ and the absorbed HCl will produce zinc chloride ($ZnCl_2$) which as a Lewis acid that can play a catalytic role in the degradation of PVC, would further accelerate degradation of PVC. When the accumulation of $ZnCl_2$ reaches a certain amount, the degradation rate of PVC will increase suddenly, making the PVC product quickly turn black. This phenomenon is called "zinc burning" [14, 15]. In order to avoid this phenomenon, $ZnSt_2$ is often used together with calcium stearate ($CaSt_2$). After $ZnSt_2$ is reacted with HCl to produce $ZnCl_2$ which can continue to react with $CaSt_2$ to form $CaCl_2$ and $ZnSt_2$. $CaCl_2$ does not catalyze the degradation of PVC, therefore inhibiting "zinc burning" over a period of time [13].

As an important organic auxiliary thermal stabilizer, some polyols, for example, pentaerythritol, sorbitol, and trimethylolpropane, etc., are often used in combination with $CaSt_2$/$ZnSt_2$ stabilizers to improve the long-term thermal stability of PVC [16]. Polyols have a large number of hydroxyl groups which can form a stable chelate with $ZnCl_2$ to inhibit its further catalytic degradation of PVC. In previous studies, we reported the synthesis of lanthanum-pentaerythritol alkoxide [17], and aluminum-pentaerythritol alkoxide [18], and their improved performances for the thermal stability of PVC. However, most polyols-based metal alkoxides have high melting points, which make themselves less dispersible in PVC. In addition, polyols have a certain degree of water solubility, resulting in poor miscibility with PVC and poor

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PVC plasticization. The presence of these drawbacks limits the widespread use of polyols-based metal alkoxides.

In this study, mannitol stearate ester (MSE) was synthesized through a direct esterifying reaction between mannitol and stearic acid, then the mannitol stearate ester-based aluminum alkoxide (MSE-Al) was prepared through the alcohol exchange reaction between MSE and aluminum isopropoxide [19, 20]. Compared to pentaerythritol, mannitol has a lower melting point of 166 °C and possesses a greater number of hydroxyl groups per unit mass. The design idea was just to improve the lubricity and reduces the melting point of MSE-Al to obtain a better compatibility with PVC by introducing stearate functional group. The results of thermal stability test further indicated that MSE-Al can provide tri-functional additive roles, namely thermal stabilizer, plasticizer and lubricant.

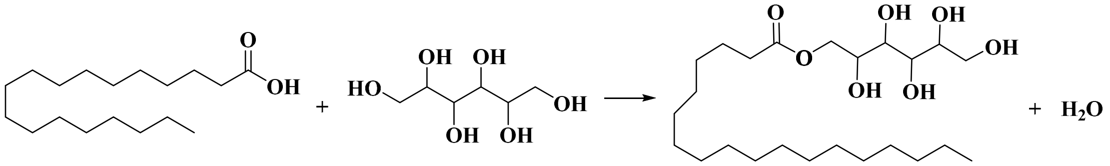
2. Experimental

2.1. Materials

PVC resin (average polymerization degree of 1005) was purchased from China Petrochemical Qilu Co. Ltd. Stearic acid and aluminum isopropoxide, D-Mannitol were all of the analytical reagent grade and obtained from Shanghai Macklin Biochemical Co., Ltd., China. $ZnSt_2$ and other additives of PVC were supplied by Shandong Huike Additives Co., Ltd., Shandong province, China. Ethanol, tetrahydrofuran (THF), cyclohexane, dioctyl phthalate (DOP) and other chemical reagents were all of analytical reagent grade.

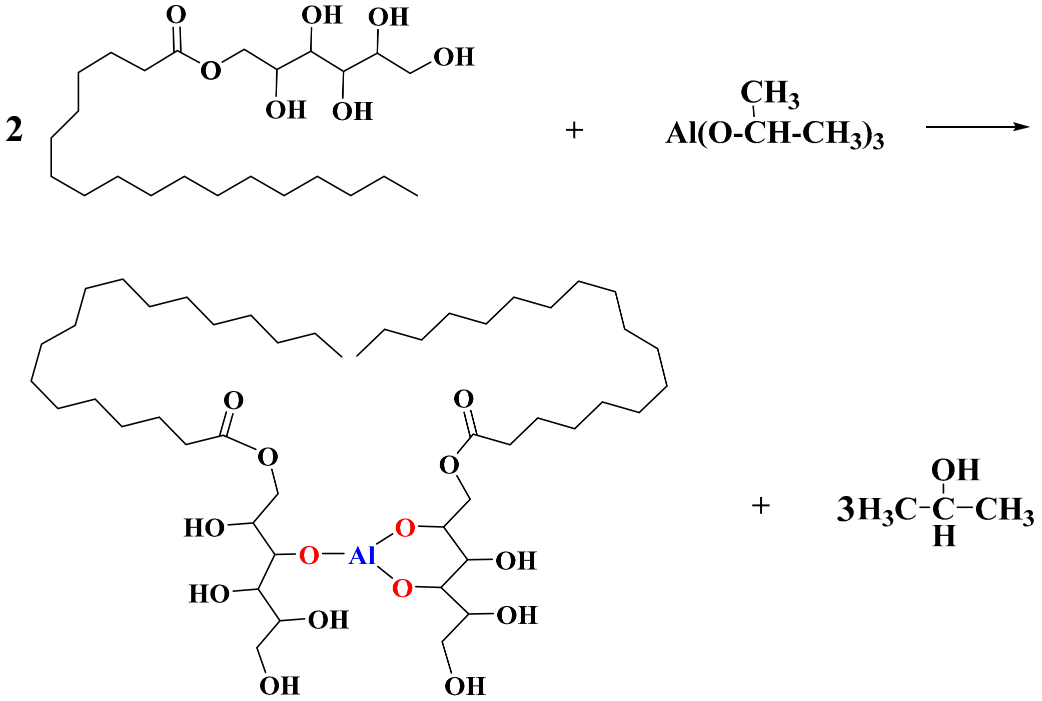
2.2. Preparation of MSE and MSE-Al

MSE was prepared through a direct esterifying reaction between D-Mannitol and stearic acid. Stearic acid (0.1 mol, 28.4 g) and D-Mannitol (0.1 mol, 18.2 g) were mixed together with 0.3 g p-toluenesulfonic acid (used as a catalyst) in a mixer set. Then the mixture and 10 ml of cyclohexane (used as water-carrying agent) were put into a three-necked round bottom flask equipped with a water separator and an electric stirrer. The mixture was heated at 170 ºC for 4 h under nitrogen atmosphere. After evaporating cyclohexane, the MSE was removed and ground into powders. Then they were put into a vacuum oven and dried for 12 h at 45 ºC. **Scheme 1** illustrates the synthesis pathway of MSE.



Scheme 1. Synthesis pathway of MSE

MSE-Al was prepared by the alcohol exchange reaction between MSE and aluminum isopropoxide. MSE (20 mmol, 8.97 g) and aluminum isopropoxide (10 mmol, 2.04 g) were dissolved in 100 mL absolute ethanol in a 250 mL three-necked round bottom flask equipped with a magnetic stirrer and a condenser-Allihn type. The mixed solution was heated to 140 °C with stirring and refluxing under nitrogen atmosphere for 3 h, and then MSE-Al was obtained by evaporating the solvent. The white solid was put into a vacuum drying oven and fully dried for 8 h at 45 °C, then grounded into powder for later use. **Scheme 2** illustrates the synthesis pathway of MSE-Al.



Scheme 2. Synthesis pathway of MSE-Al

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2.3. Characterization of MSE and MSE-Al

Fourier-Transform Infrared (FT-IR) spectra of MSE and MSE-Al were obtained on a Nicolet 5700 spectrometer by the KBr disc method. The spectrum range is 4000-400 cm^{-1} with 120 scans at a resolution of 4 cm^{-1}. Thermal gravimetric analysis (TGA) of MSE-Al was carried out by a Netzsch STA 449C at a heating rate of 10 ºC/min from 25 to 800 ºC under nitrogen flow (20 mL min^{-1}).

2.4. Preparation of PVC samples

The PVC master batch consisted of 100.0 g of PVC, 20.0 g of $CaCO_3$, 9.0 g of chlorinated polyethylene (CPE), 4.0 g of TiO_2, 2.5 g of dioctylphthalate (DOP), 2.0 g of acrylics copolymer (ACR) and 1.6 g of stearic acid (HSt), which were mixed together with 4.0 g of thermal stabilizers in a mixer set. Then the mixture was rolled using an open twin roller (XH-401, Dongguan Xihua Testing Machine Co., Ltd.) for 5 min at 180 ºC. The thickness of pressed PVC sheets was about 1.0 ± 0.1 mm.

2.5. Thermal stability test of MSE-Al

2.5.1. Congo red test

According to the standard of ISO 182-1-1990 [21], approximately 2 g of PVC samples cut into 2 mm squares were put into a test tube in which the wet Congo red paper was placed about 2.0 cm over the sample. The test tube bottom was immersed into an oil bath at 180 ºC, during which the oil was ensured to be higher than PVC samples. The time that Congo red test paper began to turn blue was defined as the thermal stability time (ΔT).

2.5.2. Conductivity measurement

2 g of PVC samples cut into squares of 2.0 mm × 2.0 mm were placed in the reaction vessel heated at 180 ºC. Nitrogen (about 7 L/h) was introduced into the reaction vessel and blown out from the outlet, then was passed into 60 mL of deionized water. The HCl gas formed from the thermal degradation of PVC would be carried by the nitrogen gas and absorbed by the deionized water, resulting in the conductivity of the water changed with respect to time [6]. The change of conductivity reflected the degradation rate of PVC. The conductivity meter used to

measure the conductivity of solution was made by Shanghai INESA Scientific Instrument Company Limited, China (DDS-307).

2.5.3. Thermal aging test

According to the ISO 305-1990 (E) standard [22], PVC samples were cut into 15 mm × 15 mm squares and placed into a thermal aging test box at 180 ± 2 ºC in air. The samples were removed every 10 min, and the color changes of PVC samples were observed and compared, which reflected thermal stability of the thermal stabilizers on PVC.

2.5.4. UV-vis spectroscopy test

With the HCl releasing during the thermal degradation of PVC, a conjugated double bond structure is simultaneously produced. The length and concentration of the conjugated double bond in PVC can be characterized by the wavelength and the height of the absorption peak in the UV-vis spectrum, which was measured by the UV-visible spectrometer (UV-2450PC, Shimadzu Scientific Instruments, Japan) with the slit width set at 2 nm over the wavelength in the range of 200-400 nm.

0.02 g of PVC sample was soaked in 50 mL of freshly distilled tetrahydrofuran for one week, and then, shaken with an ultrasonic extractor for 30 min. After filtration, the supernatant was detected using an UV-visible spectrometer.

2.5.5 Torque rheometer test

According to the ASTM D 2538-79 standard, the impact of MSE-Al on the dynamic rheological property of PVC was investigated by torque rheometer (RM-200C, Harbin Harp Electric Technology Co., Ltd., China). The torque rheometer operating temperature was set to 180 ºC with keeping a rotor speed of 35 rpm.

2.6. The capacity for neutralizing HCl

Conductometric titration experiments were carried out to investigate the capacity of stabilizers to neutralize HCl. 6.00 mL of 0.1 mol/L HCl standard solution was diluted with 20.00 mL of ethanol and 10.00 mL of deionized water. 0.0500 g of MSE-Al, lead salts, and $ZnSt_2$ were dissolved in this solution with a magnetic stirring at 40 ºC. The excess HCl solution was back-titrated with 6.00 mL of 0.1 mol/L NaOH standard solution. The conductivity of the solution was measured by a conductivity meter (DDS-307, Shanghai INESA Scientific Instrument Company Limited, China). The volume of NaOH solution corresponding to the minimum conductivity of the solution was the titration endpoint, and the capacity for neutralizing HCl could be calculated by the volume of NaOH solution used.

3. Results and discussion

3.1. Characterization of MSE-Al

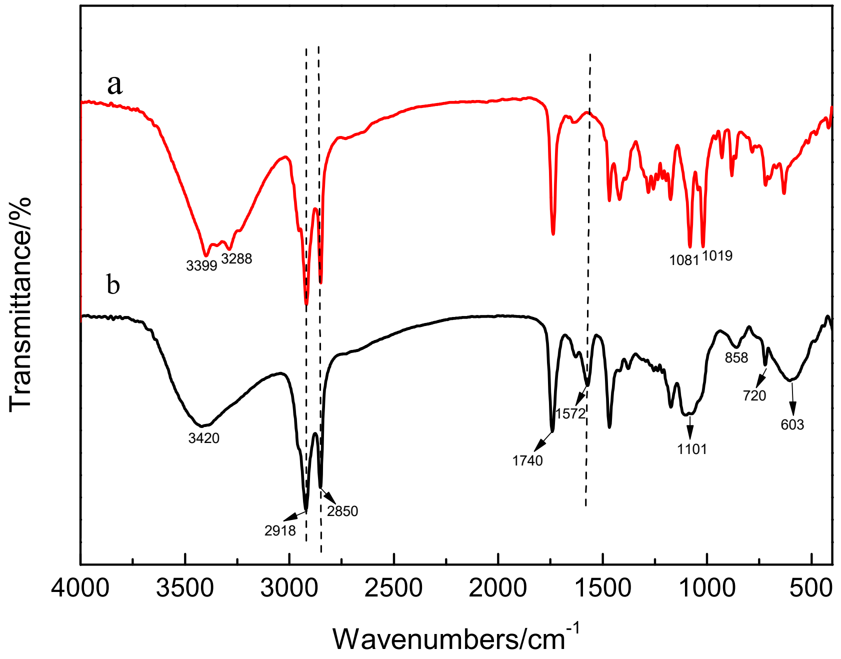

Fig. 1. FTIR spectra of (a) MSE and (b) MSE-Al

The FT-IR spectra of MSE and MSE-Al are shown in Fig. 1. There are obvious absorption peaks in both spectra at the range of 3200 to 3500 cm^{-1}, which correspond to –OH stretching vibration. Two peaks in spectrum (a) at 1081 and 1019 cm^{-1} are belong to –OH bending vibration in MSE. As shown in Fig. 1, the peaks at 2920 and 2851 cm^{-1} can be assigned as the C–H stretching vibration, and the peaks at 1467 and 1377 cm^{-1} arise from the bending vibrations of $-CH_2$ and $-CH_3$, respectively. And in Curve (b), an intense peak appears at about 1572 cm^{-1} in MSE-Al which also shows in aluminum isopropoxide (metal alkoxides) corresponding to C–O bands [23]. The peaks at 1740 cm^{-1} in both spectra ((a) and (b)) are attributed to C=O stretching vibration of the ester group, indicating that there exist ester groups on MSE and MSE-

Al. The peak at 720 cm^{-1} belongs to in-plane rocking vibration of $-(CH_2)_n-$, (n>4). M. Khosravi et al. suggested that C-O-Al bond stretch of aluminum alkoxides appears at 1030-1080cm^{-1} [24]. Curve (b) also shows that the characteristic peak of C-O-Al bond is superimposed with the two peaks at 1081 and 1019 cm^{-1} as in spectrum (a). The broad peak around 603 cm^{-1} in spectrum (b) is attributed to the characteristic absorption of Al–O bond in MSE-Al [23], which confirms the formation of mannitol stearate ester-based aluminum alkoxides (MSE-Al).

3.2. Thermal analysis of MSE-Al

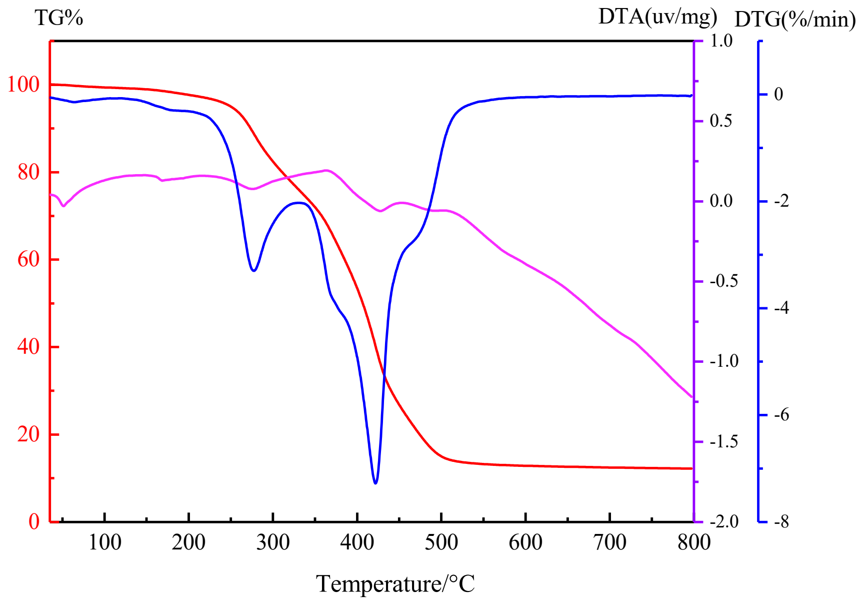

Fig. 2. TGA, DTG and DTA curves of Al-Mse

Comparative techniques of thermal analysis were used to evaluate the heat resistance of MSE-Al in a nitrogen atmosphere. TGA, DTG and DTA curves of MSE-Al are shown in Fig. 2. There is no apparent weight-loss from 25 to 230 ºC in the TGA and DTG curves. An endothermic peaks can be observed at about 51 ºC in this range, which means that the melting point of MSE-Al is about 51 ºC. This result suggested that MSE-Al has an excellent stability and dispersion at the processing temperature (about 180 ºC) of PVC. As shown in Fig. 2, the first weight-loss step occurs in the range of 240-340 ºC, and the second weight-loss step occurs in the range of 350-600 ºC. After 800 ºC, MSE-Al was decomposed into black residue containing zinc oxide and carbon residue with a weight percentage of 12.22%.

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3.3. Thermal stability tests of MSE-Al on PVC

3.3.1 Appropriate dosage of MSE-Al

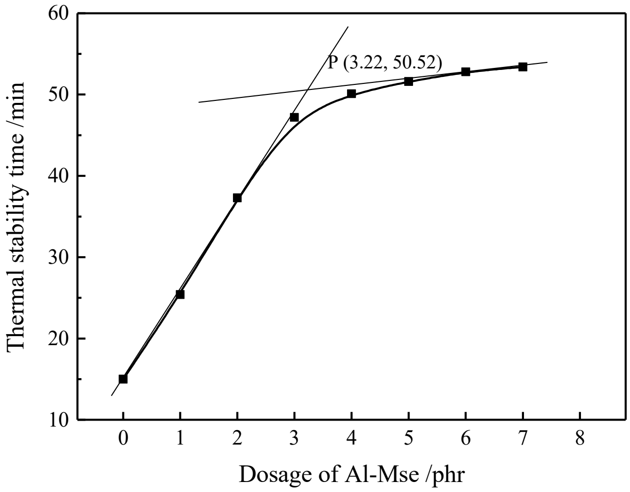

Fig. 3. Thermal stability time of the PVC samples stabilized with different amounts of MSE-Al

PVC sample heated in 180 °C will release hydrogen chloride. When the concentration of HCl reaches a certain value, HCl will make the Congo red paper at the top of PVC sample to turn blue. The time when Congo red paper starts to turn blue was defined to be the thermal stability time (ΔT). In order to determine the optimal dosage of MSE-Al, the stability tests were performed on PVC samples stabilized with different dosage of MSE-Al. As shown in Fig. 3, the ΔT of pure PVC is only 15 min. With the increase of MSE-Al, the ΔT of PVC was gradually prolonged. These results indicated that MSE-Al is able to effectively improve the stability of PVC. However, as the dosage of MSE-Al increased to a certain amount, the ΔT of PVC stabilized with more MSE-Al almost would not increase. The optimum amount of MSE-Al was determined by intersection of the two extrapolations. Fig. 3 shows that the optimum amount of MSE-Al is 3.22 phr and the resulting ΔT was 50.52 min. For comparison with other thermal stabilizers, the dose of MSE-Al was set at 4 phr in this study.

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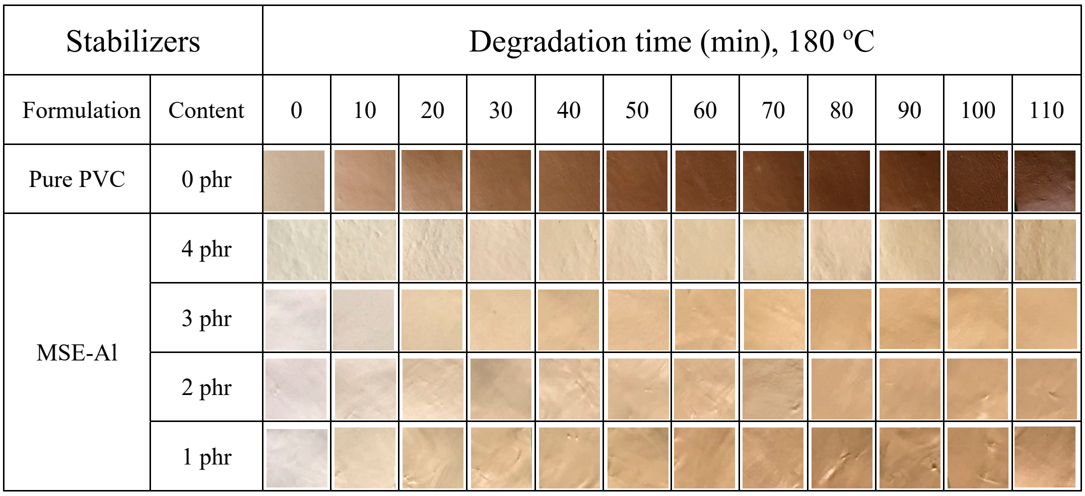
3.3.2 Oven aging test of MSE-Al on PVC



Stabilizers		Degradation time (min), 180 ºC											
Formulation	Content	0	10	20	30	40	50	60	70	80	90	100	110
Pure PVC	0 phr												
MSE-Al	4 phr												
	3 phr												
	2 phr												
	1 phr												

Fig. 4. Thermal aging test of PVC samples stabilized with different amounts of MSE-Al

The results of Oven thermal aging test of PVC sheets containing different dosage of MSE-Al are shown in Fig. 4. It can be seen that the color of the pure PVC sample starts to turn yellow during the process, and quickly turns to brown and then to black over time with heating at 180 ºC. Moreover, the addition of MSE-Al can significantly improve the thermal stability of PVC, and the more the content of MSE-Al, the better the thermal stability of the PVC samples. This implied that MSE-Al can be an excellent long-term thermal stabilizer for PVC. However, the initial color of PVC sheets stabilized with MSE-Al was not very ideal. So, in the following studies, MSE-Al was compounded with $ZnSt_2$ to improve the initial whiteness of PVC and to reduce the cost.

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3.4. Thermal stability tests of MSE-Al/ZnSt$_2$ on PVC

3.4.1. Congo red test

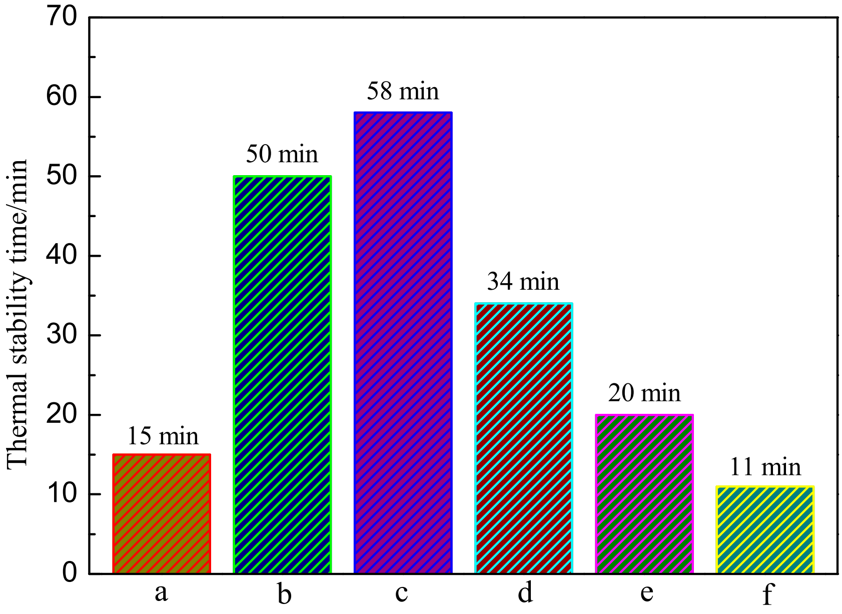

Fig. 5. Thermal stability time of pure PVC and PVC stabilized by MSE-Al/ZnSt$_2$ at the content of 4 phr in 180 °C. a, pure PVC; b, 4 phr MSE-Al; c, 3 phr MSE-Al + 1 phr ZnSt$_2$; d, 2 phr MSE-Al + 2 phr ZnSt$_2$; e, 1 phr MSE-Al + 3 phr ZnSt$_2$; and f, 4 phr ZnSt$_2$.

Fig. 5 shows the Congo red test results of pure PVC and PVC samples with different ratios of MSE-Al and ZnSt$_2$. The ΔT of pure PVC was only 15 min. ΔT of the PVC sample with addition of 4 phr of MSE-Al increased to 50 min, which indicated that MSE-Al could obviously improve the thermal stability of PVC. The ΔT of PVC samples added with 3 phr of MSE-Al and 1 phr of ZnSt$_2$ was 58 min, showing an obvious synergistic effect between MSE-Al and ZnSt$_2$. Fig. 5 also suggests that, with the increase of ZnSt$_2$, the thermal stability time of PVC samples decreases obviously, showing that MSE-Al plays a critical role in improving the long-term thermal stability of PVC. As the amount of ZnSt$_2$ increased to 4 phr, the ΔT was 11 min, even shorter than the thermal stability time of pure PVC, indicating that “zinc burning” might have occurred, which accelerated the degradation of PVC.

3.4.2. Conductivity test

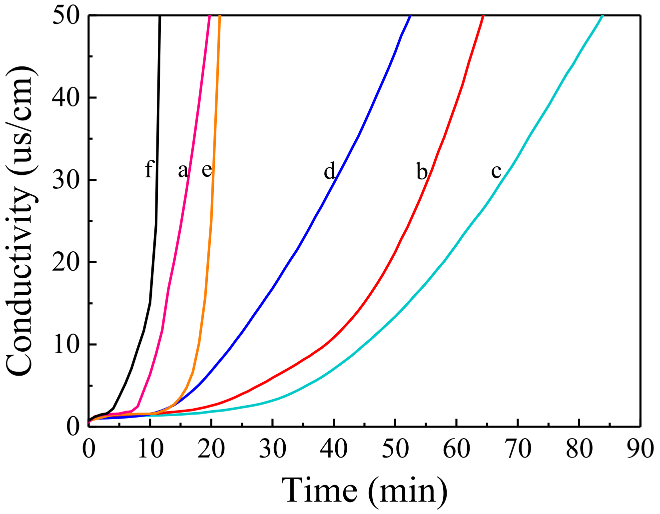

Fig. 6. Conductivity versus time plots for pure PVC (a); and PVC stabilized by 4 phr of MSE-Al (b); MSE-Al/ZnSt$_2$ (3:1) (c); MSE-Al/ZnSt$_2$ (2:2) (d); MSE-Al/ZnSt$_2$ (1:3) (e); and ZnSt$_2$ (f).

Table 1. Induction time and stabilization time for different PVC samples

Stabilizers		Induction time (min)	Stabilization time (min)
MSE-Al (phr)	ZnSt$_2$ (phr)		
/	/	12.7	19.9
4	/	46.3	64.3
3	1	49.5	84.1
2	2	25.2	52.4
1	3	17.8	21.5
/	4	10.3	11.7

The HCl produced during the thermal degradation of PVC was carried into the deionized water by nitrogen gas. The conductivity of the deionized water was tested and recorded by a conductivity meter to obtain a curve of the conductivity vs. time. The time from the start of heating to the point where the conductivity begins to change is called the induction time (T_i). The time when the conductivity of deionized water increased to 50 µs/cm was called the thermal stabilization time (T_s) of PVC [17]. Fig. 6 shows the conductivity test results of pure PVC and PVC samples with

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different ratios of MSE-Al and $ZnSt_2$. The T_i and T_s of PVC samples are also listed in Table 1. As shown in the Curve (a) of Fig. 6, the T_i and T_s of pure PVC samples are 12.7 min and 19.9 min, respectively. The T_i and T_s of PVC stabilized with 4 phr of MSE-Al increased to 46.3 and 64.3 min, respectively. This means that MSE-Al might be able to neutralize the HCl produced during the degradation of PVC or inhibit the production of HCl. Curve (c) is the conductivity curve of the PVC samples stabilized with 3 phr of MSE-Al and 1 phr of $ZnSt_2$, which has the longest T_i and T_s, 49.5 and 84.1 min, respectively. It indicated that there was a strong synergistic effect between MSE-Al and $ZnSt_2$. However, with the further increase dosage of $ZnSt_2$, the thermal stability of PVC decreased significantly, and when stabilized with pure 4 phr of $ZnSt_2$, the thermal stability of PVC was even worse than pure PVC. This result also proved that the use of pure zinc stearate as a PVC heat stabilizer would catalyze the thermal degradation rate of PVC.

3.4.3. Thermal aging test

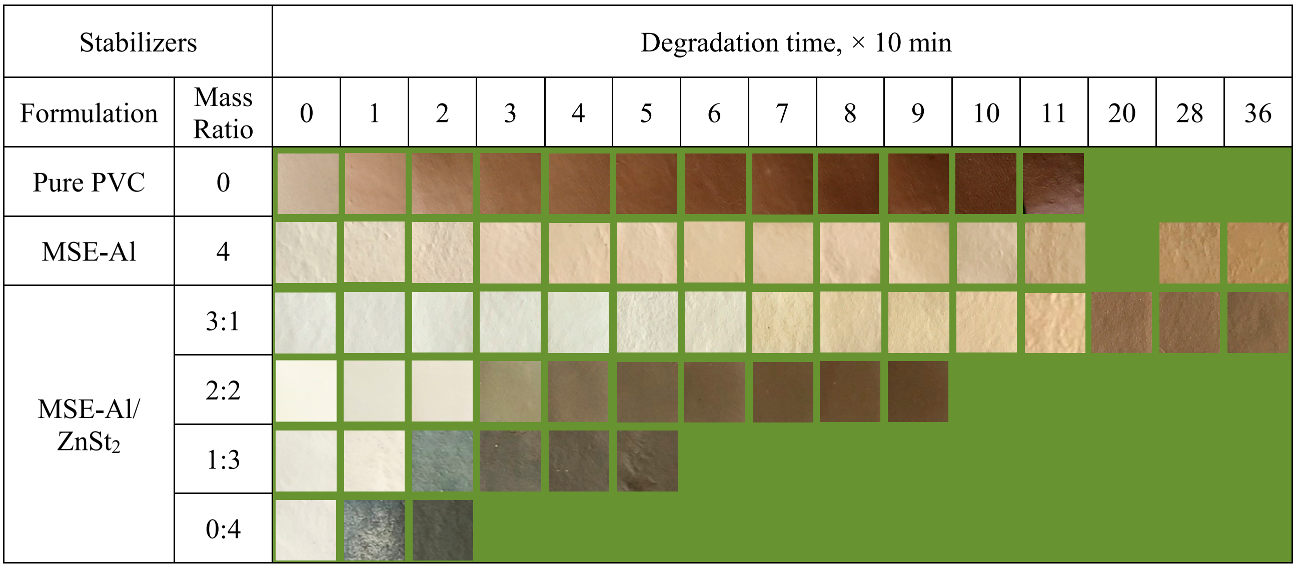

Fig. 7. Results of thermal aging tests for pure PVC and PVC stabilized by 4 phr of MSE-Al or different mass ratios of MSE-Al and $ZnSt_2$ when heated at 180 °C in an oven.

In the process of PVC thermal degradation, HCl is released and conjugated double bonds are formed simultaneously. With the extension of heating time, the amount conjugate double bonds is further increased. When the conjugate structure reaches a certain scale, the PVC begins to change color. Generally speaking, the color of PVC changes continuously from white to yellow, brown, and finally black. Fig. 7

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shows the results of thermal aging test of PVC sheets containing different mass ratios of MSE-Al and $ZnSt_2$ stabilizers. The color of the pure PVC samples started to turn yellow during the process of preparing the PVC sheet with the double roll mill, and quickly turned to brown with heating at 180 °C. As shown in Fig. 7, the PVC sheets added with 4 phr of MSE-Al showed a very light pale yellow initial color and would keep the color stable within 110 min, and do not turn black within 360 min, meaning that MSE-Al has an excellent long-term thermal stability on PVC. It can be seen from Fig. 7 that the PVC sheets with 3 phr of MSE-Al and 1 phr of $ZnSt_2$ show the best initial color and a good long-term stability. The color do not turn black within 110 min, indicating that there is a good synergistic effect between MSE-Al and $ZnSt_2$ on the initial color and the long-term thermal stability of PVC. Fig. 7 also shows that, if there is $ZnSt_2$ in the formula of thermal stabilizers, PVC has good initial whiteness, but the long-term thermal stability is getting worse with the increase of $ZnSt_2$. Even more, when the dosage of $ZnSt_2$ increased to 3 phr or 4 phr, the PVC sheets began to experience "zinc-burning" phenomenon. The above results indicated that MSE-Al mainly played a role in improving the long-term thermal stability of PVC, while $ZnSt_2$ mainly contributed to improving the initial whiteness of PVC.

3.4.4. UV-vis spectroscopy test

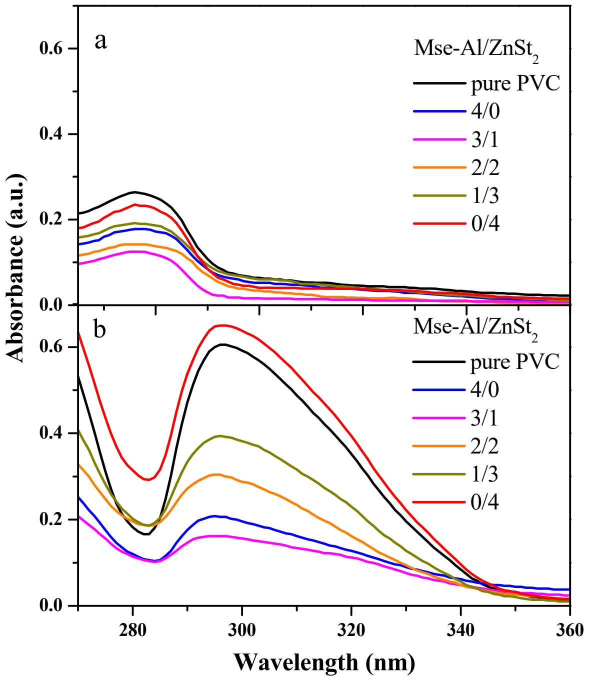

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Fig. 8. UV–vis spectra of PVC samples stabilized with no stabilizer or with different mass ratios of thermal stabilizers heated for 0 min (a) and 90 min (b) at 180 ºC.

Absorbance of UV–vis spectra represents the concentration of conjugated double bonds (C_{db}), and the position of absorption peak indicates the length of conjugated chain. Fig. 8 displays the UV–vis spectra of pure PVC samples and PVC stabilized with different mass ratios of thermal stabilizers heated at 180 ºC for 0 or 90 min. Fig. 8a shows that the maximum absorption peak of the six PVC samples is at near about 275 nm, indicating that the dehydrochlorination of PVC produced a conjugated triene structure. Pure PVC has the highest peak height and the C_{db} of pure PVC is the biggest, showing that the initial color of pure PVC maybe the worst. The smallest was the PVC stabilized with 3 phr of MSE-Al and 1 phr of $ZnSt_2$, indicating that PVC stabilized with this component own the best initial color which was consistent with the results of the thermal aging test.

Fig. 8b shows the UV–vis spectra of PVC samples heated at 180 ºC for 90 min. The maximum absorption peak of the six PVC samples shifts to near 300 nm, indicating that PVC samples further decompose to generate a conjugated tetraene structure. Fig. 8b also shows that, except that the C_{db} of PVC stabilized with 3 phr of MSE-Al and 1 phr of $ZnSt_2$ was remained unchanged, all the other C_{db} of PVC samples changed greatly. Especially, the C_{db} of pure PVC and PVC stabilized with 4 phr of $ZnSt_2$ were more than twice the original. The lowest C_{db} of the PVC sample stabilized with 3 phr of MSE-Al and 1 phr of $ZnSt_2$ indicated that this mass ratio (3:1) of MSE-Al and $ZnSt_2$ had the best synergistic effect. With the further increase of $ZnSt_2$ dosage, the C_{db} of PVC samples gradually increased, indicating that, as the amount of $ZnSt_2$ increased, the degree of thermal degradation of PVC increased. It is also found that the C_{db} of PVC samples stabilized with 4 phr of $ZnSt_2$ was higher than that of the pure PVC, which indicated that the PVC sample might have occurred "zinc burning" phenomenon.

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3.4.5. Torque rheometer test

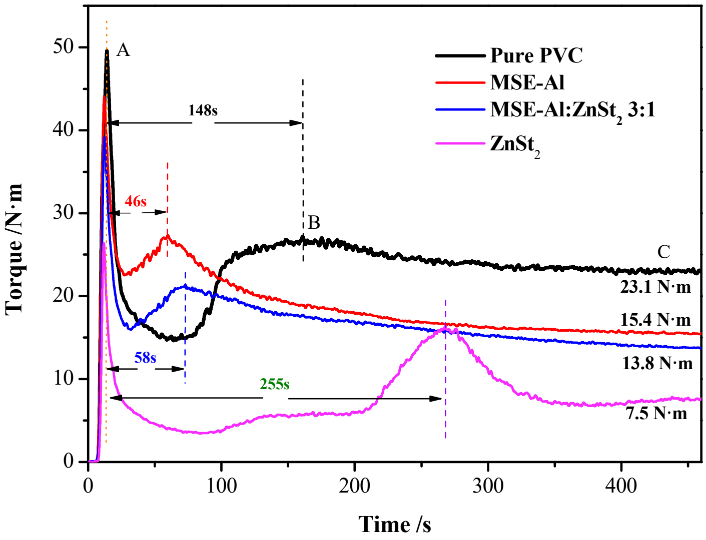

Fig. 9. Results of time dependent torque rheology test obtained at 180 °C and 50 rpm rotation rate for pure PVC and PVC stabilized by 4 phr of different thermal stabilizers

Fig. 9 is the torque rheometer curves of pure PVC and PVC samples stabilized by 4 phr of different thermal stabilizer. In the rheological curve (Fig. 9), point A is the filler torque peak, and the greater the torque, the greater the friction of PVC mixture just entering the mixing chamber of torque rheometer. Point B is the plasticizing torque peak, and its corresponding time indicates the plasticizing effect and difficulty of PVC mixture. Point C is the balance torque and represents the processing performance (lubricating property) of the PVC mixture. Fig. 9 shows that the filler torque values and balance torque values of the PVC samples stabilized by MSE-Al and $ZnSt_2$ are much lower than that of pure PVC. It was worth noting that the PVC sample stabilized by 4 phr of $ZnSt_2$ had the lowest balance torque, showing that $ZnSt_2$ had the best lubricity for PVC. The balance torque of the PVC sample stablized by 4 phr of MSE-Al was much lower than that of pure PVC. All of the results showed that MSE-Al and $ZnSt_2$ had good lubrication. This might be due to the presence of stearic acid radical functional group in MSE-Al and $ZnSt_2$ which gave MSE-Al and $ZnSt_2$ good lubricity.

Fig. 9 also indicates that PVC stabilized by MSE-Al has a plasticizing peak that is 102 s shorter than that of the other PVC samples, showing that MSE-Al has the best

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excellent plasticizing function. Generally speaking, most of the common plasticizers of PVC are esters, such as phthalate esters [25]. The esters acting as cohesive blocks could increase the compatibility with PVC [26]. For example, Van Oosterhout et al. reported that plasticizers could act as solvents for amorphous regions of PVC, thus the PVC chains in the amorphous regions might become solvated during processing [27]. Therefore, the good plasticizing effect MSE-Al on PVC is because that MSE-Al has the mannitol stearate ester acting as an efficient plasticizing functional group. The plasticizing time of PVC stabilized by 4 phr of $ZnSt_2$ was 255 s, longer than that of pure PVC, indicating that $ZnSt_2$ has no plasticizing effect on PVC. In addition, PVC samples stabilized by MSE-Al/$ZnSt_2$ (3:1) had excellent plasticizing performance and suitable lubricity, indicating that there was a good synergistic effect between MSE-Al and $ZnSt_2$ (3:1) on plasticizing and lubricity.

3.5. Thermal stabilizing mechanism of MSE-Al

Metal alkoxides are strong alkalis and good nucleophile. The ability of metal alkoxides to neutralize HCl is strong, but they are not suitable to be used as PVC thermal stabilizers due to their easy hydrolysis [28]. However, MSE-Al was a polyol ester-based metal alkoxides which cannot be easily hydrolyzed due to the property of polyhydric hydroxyl metal alkoxides and the introduction of stearate, and then can act as a thermal stabilizer for PVC.

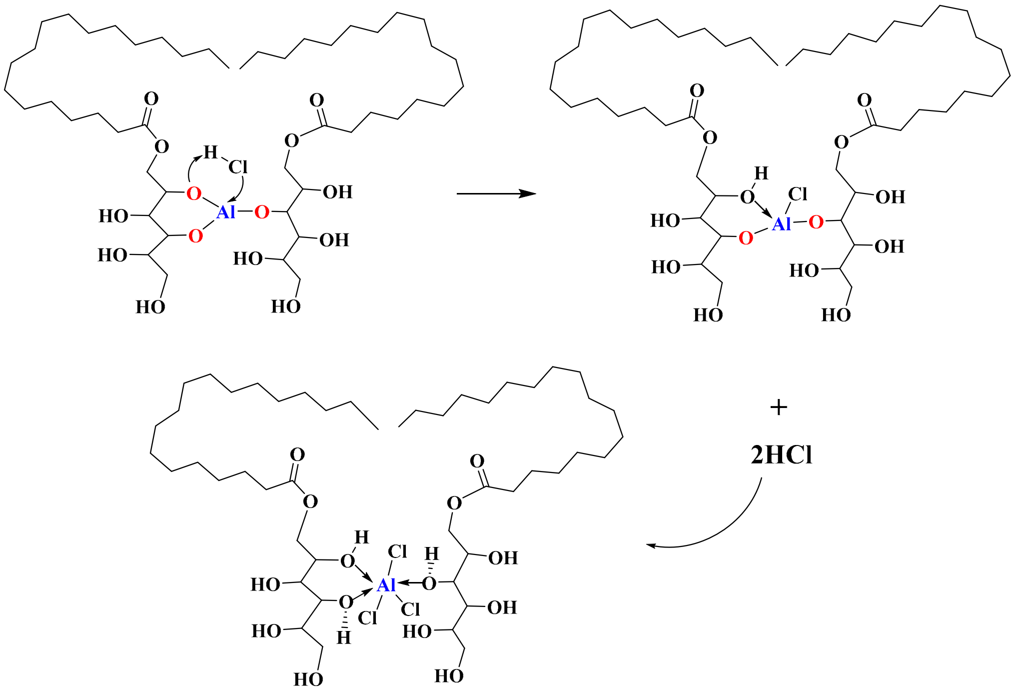
3.5.1 Neutralize HCl

One of the main functions of MSE-Al as a PVC thermal stabilizer is to neutralize HCl. In order to investigate the ability of MSE-Al to absorb HCl, a conductometric titration experiment [29] was used to compare with lead salts and $ZnSt_2$. As shown in Table 2, the capacity of MSE-Al to absorb HCl is distinctly lower than that of lead salts and $ZnSt_2$, indicating that the main role of MSE-Al to protect PVC might react with the unstable chlorine atom in the PVC chain to prevent the degradation of PVC, just as the other polyol-based metal alkoxides [30].

Table 2. HCl absorption capacity of the PVC thermal stabilizers

Stabilizer	HCl absorption capacity (1g of thermal stabilizer absorbs the mass of HCl)
Lead salt	278.50 mg
$ZnSt_2$	95.38 mg
MSE-Al	61.95 mg

Based on the results it was deduced that MSE-Al as a PVC thermal stabilizer can be used for neutralizing HCl through the equation in **Scheme 3**.



Scheme 3. The pathway for MSE-Al neutralizing HCl

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3.5.2 Replacement of the labile chlorine atoms in the PVC

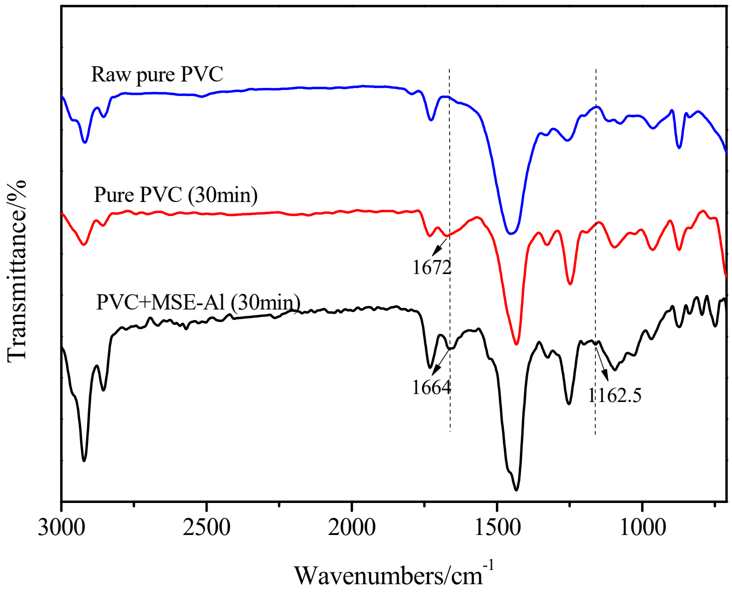
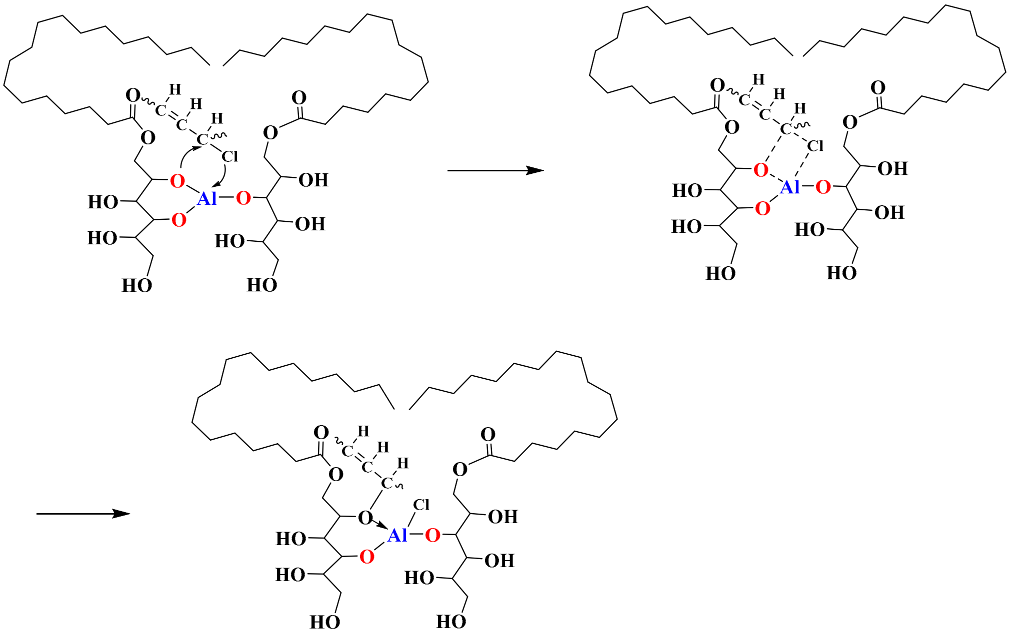


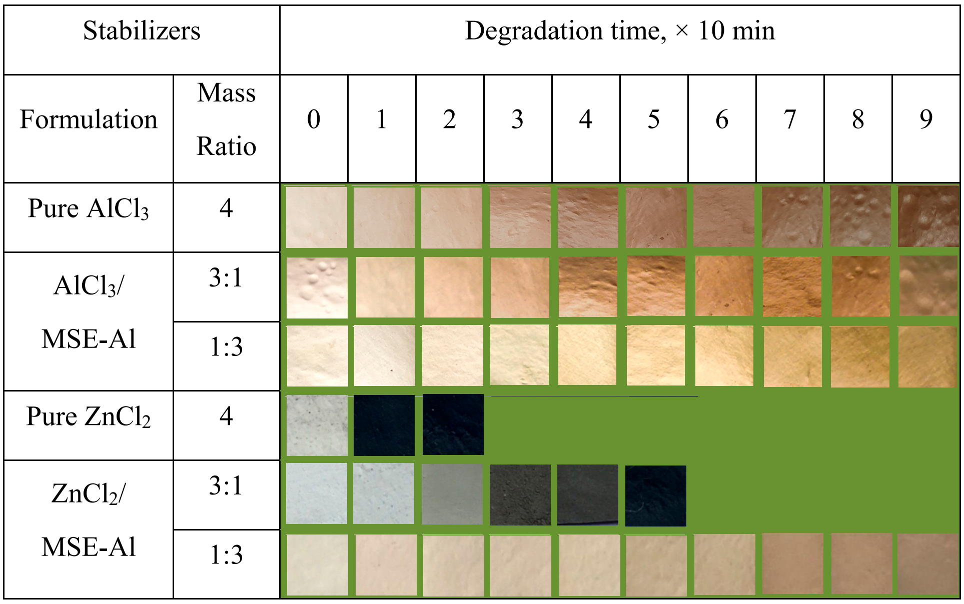
Fig. 10. FTIR spectra of pure PVC and PVC stabilized by 4 phr of MSE-Al (heated at 180 °C for 30 min)

Due to the presence of high electronegative alkoxy groups, MSE-Al has a tendency to undergo nucleophilic reactivity, and can replace the labile chlorine atoms in the PVC [30]. Fig. 10 shows the FTIR spectra of pure PVC and PVC samples stabilized by MSE-Al. After having been heated at 180 °C for 30 min, both the pure PVC and PVC sample stabilized by MSE-Al have a stretching vibration peak of C=C at about 1672 cm^{-1}, suggesting that PVC degrades to form a conjugated double bond. Compared with the pure PVC sample, a new peak appeared at 1162.5 cm^{-1} for the PVC sample stabilized with MSE-Al which was corresponding to the stretching vibration of C-O-C [31]. These results represented that MSE-Al replaced the labile chlorine atoms in the PVC chains. The reaction between MSE-Al and labile chlorine atoms can be described by the equation in **Scheme 4**.



Scheme 4. A possible way of MSE-Al replacing the labile chlorine atoms of PVC

3.5.3 Formation of complex with $AlCl_3$ and $ZnCl_2$



Stabilizers		Degradation time, × 10 min									
Formulation	Mass Ratio	0	1	2	3	4	5	6	7	8	9
Pure $AlCl_3$	4										
$AlCl_3$/ MSE-Al	3:1										
	1:3										
Pure $ZnCl_2$	4										
$ZnCl_2$/ MSE-Al	3:1										
	1:3										

Fig. 11 Thermal aging test of PVC samples compounded with different stabilizers and heated at 180 °C.

In order to verify that MSE-Al could form a stable complex with $AlCl_3$ and $ZnCl_2$, the thermal aging test of PVC samples stabilized by pure $AlCl_3$, $ZnCl_2$, and $AlCl_3$/MSE-Al, were tested, and the results are shown in Fig. 11. The color of PVC stabilized with pure $AlCl_3$ is light gray at the beginning, and gradually changes into light brown, and dark brown at last. The results showed that although the $AlCl_3$ has no

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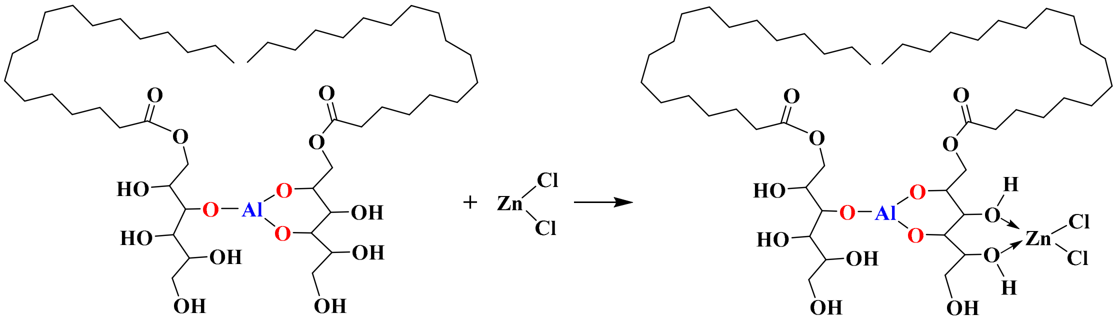
thermal stabilization effect on PVC, it did not cause “zinc-burning” phenomenon, indicating that the existence of $AlCl_3$ did not catalyze the dehydrogenation of PVC. It was the reason why the PVC stabilized with MSE-Al had excellent long-term stability effect. On the contrary, the color of PVC samples stabilized by pure $ZnCl_2$ turned into absolutely black after being heated for 10 min, showing the occurrence of “zinc-burning” phenomenon. Fig.11 also shows that the combination of $AlCl_3$/MSE-Al can inhibit PVC from turning black quickly, indicating that the complexes can form between them. The PVC samples stabilized by $ZnCl_2$/MSE-Al with mass ratio of 3:1 had light gray white in the beginning, and turned into absolutely black after heated 30 min. Furthermore, the color of PVC stabilized by $ZnCl_2$/MSE-Al with mass ratio of 1:3 did not turn into black within 90 min, suggesting that the hydroxyl of MSE-Al could form complex with $ZnCl_2$, thus suppressing the occurrence of “zinc burning”. The possible mechanism can be represented by Scheme 5. This fact also explains why there is a good synergy between MSE-Al and $ZnSt_2$.



Scheme 5. A suggestion for MSE-Al chelating $ZnCl_2$

4. Conclusion

MSE-Al was synthesized through an alcohol exchange reaction, and investigated by means of a number of characterization methods. The introduction of stearate radical reduced the melting point of the metal alkoxides, increased the dispersibility in PVC, and improved the lubricity between PVC powders. Furthermore, Torque rheometer test results demonstrated that MSE-Al is able to significantly enhance the plasticizing effect and lubricity of PVC.

The thermal stability of PVC samples stabilized with MSE-Al, and MSE-Al/ZnSt$_2$ was also evaluated by Congo red tests, conductivity measurements, thermal aging tests, and UV-vis spectroscopy tests. The results showed that MSE-Al can significantly improve the long-term thermal stability of PVC, attributed to the fact that MSE-Al replaced the labile chlorine atoms in the PVC chain and had a strong ability to neutralize HCl. A synergistic effect between MSE-Al and ZnSt$_2$ was observed. It was also found that PVC stabilized with 3 phr MSE-Al and 1 phr ZnSt$_2$ showed a good initial color and excellent long-term thermal stability. This was because ZnSt$_2$ has a strong ability to absorb hydrogen chloride, and MSE-Al would not only replace unstable chlorine atoms in the PVC chain, but also chelate the ZnCl$_2$ produced by absorption of HCl by ZnSt$_2$, thereby inhibiting the "zinc burning" phenomenon.

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