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Facile synthesis of di-mannitol adipate ester-based zinc metal alkoxide as bi-functional additives for PVC

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Abstract

A new di-mannitol adipate ester-based zinc metal alkoxide (DMAE-Zn) was synthesized as a bi-functional PVC thermal stabilizer for the first time. The materials were characterized with Fourier-transform Infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Characterization results confirmed the formation of Zn-O bonds in DMAE-Zn; and that DMAE-Zn had a high decomposition temperature and a low melting point. The thermal stability of DMAE-Zn on PVC also was tested by conductivity test, thermal aging test, and UV-visible spectroscopy (UV-VIS) test. PVC stabilized by DMAE-Zn had a good initial color and excellent long-term stability. UV-VIS also showed that the conjugated structure in PVC stabilized by DMAE-Zn was almost all of the triene, suggesting that the addition of DMAE-Zn would suppress the formation of conjugated structures above tetraene. Dynamic processing performance of PVC samples tested by torque rheometer indicated that, having a good compatibility with PVC chains in the amorphous regions, DMAE-Zn contributed good plasticizing effect to PVC. DMAE-Zn thus effectively demonstrates bi-functional roles, e.g., thermal stabilizers and plasticizers to PVC. Furthermore, FT-

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IR, HCl absorption capacity test, and complex $ZnCl_2$ test were also used to verify the thermal stability mechanism of DMAE-Zn for PVC.

Key words: PVC; thermal stabilizers; bi-functional; di-mannitol adipate ester-based zinc metal alkoxide; plasticizers

1. Introduction

Poly (vinyl chloride) (PVC) is one of the five general plastics, has been widely used in infrastructure construction and home supplies because of its excellent low-cost, high strength, corrosion resistance, and self-extinguishing, etc.[1] In the applications the poor thermal stability is the biggest weakness of PVC. When the temperature reaches 130 ºC or higher, PVC starts to break down and release hydrogen chloride (HCl), which can further aggravate this degradation process[2]. The color of PVC will change significantly from white to brown, and finally black, meanwhile mechanical properties also decline rapidly [3]. Therefore, thermal stabilizers must be added during the PVC processing to inhibit the production of HCl and remove the free HCl[4].

At present, lead salts, metal soap, and organotin are the mainstream thermal stabilizers. Although lead salts have the best thermal stability for PVC, the toxicity restricts their application. Metal soap, such as calcium stearate ($CaSt_2$), and zinc stearate ($ZnSt_2$), has no toxicity, but the thermal stabilizing effect on PVC is not ideal, especially the "zinc-burning" will lead to rapid degradation of PVC [5-10]. Organotin has an excellent thermal stability on PVC, but the cost of is too high[11]. It is then necessary to develop new non-toxic and efficient thermal stabilizer of PVC[12-14].

A number of new types of thermal stabilizers, for example, zinc and calcium salts of 11-maleimideoundecanoic acid, liquid Ca/Zn thermal stabilizer synthesized, zinc and calcium oxolinic complexes, ricinoleic acid-based Ca/Zn stabilizer, have been reported [11, 13, 15-19]. Some researchers also indicated that polyols can serve as auxiliary thermal stabilizers. Having many hydroxyl groups, polyols are able to chelate $ZnCl_2$ to inhibit the "zinc burning" phenomenon[3, 20]. Jenneskens et al. found that the natural polyols can significantly improve the thermal stability of PVC [21, 22].

Guo et al. reported that the addition of pentaerythritol combined with $CaSt_2/ZnSt_2$ would improve the thermal and color stability of PVC [23].

Recently, we have synthesized a series of polyols-based metal alkoxides as PVC thermal stabilizers, and showed that they were efficient in inhibiting the degradation of PVC [24, 25]. There is still a challenge for these polyols-based metal alkoxides to be used as PVC thermal stabilizers, because their melting point (about 220 ºC) [1, 2] are significantly higher than the processing temperature of PVC, affecting their consistency with PVC [26]. In order to reduce the melting point of the polyol-based metal alkoxides, Shentu et al. employed mannitol with a low melting point of 166 ºC to synthesize mannitol-zinc metal alkoxides, which was then used to improve PVC thermal stability [2]. New strategy has been applied by our group to overcome this shortcoming by esterification. For example, we synthesized the pentaerythritol stearate ester-based zinc alkoxides (PSE-Zn) [26] and cis-1,2-cyclohexanedicarboxylic acid di-mannitol ester-based zinc metal alkoxides [27]. We observed that the new ester-based alkoxides have a lower melting point and good thermal stabilization performance on PVC.

Generally speaking, plasticizer, one of the most important PVC processing aids, is to be added to adjust the mechanical and thermal properties of PVC. Phthalate esters are the most commonly used plasticizers in PVC processing. However, most of the phthalate plasticizers are well-known to be toxic [28]. More and more researchers are committed to developing new non-toxic PVC plasticizers. It is recommended to use sustainable alternative instead of phthalate esters. Epoxidized vegetable oils are one of the alternatives [28, 29].

In this study, a new kind of thermal stabilizers, di-mannitol adipate ester-based zinc metal alkoxide (DMAE-Zn), were synthesized, and characterized by Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis. Their thermal stability performances on PVC also were tested through oven aging method, conductivity test, UV-VIS spectroscopy test, and torque rheometer test. It was found that DMAE-Zn can effectively play bi-functional roles of being both a thermal stabilizer and a plasticizer to PVC.

2. Experimental

2.1. Materials

PVC resin (type SG-5, average degree of polymerization: 1005, viscosity number: 67) was from Petrochemical Qilu Limited Co., China. Some additives of thermal stabilizers were kindly supplied by Shandong Huike Additives Co., China. D-mannitol, pentaerythritol, glycerol, adipic acid, phosphoric acid, cyclohexane, absolute ethanol, zinc acetate and other chemical agents were all of analytical grade.

2.2. Preparation process

2.2.1 Preparation of di-maltitol adipate ester

Di-mannitol adipate ester (DMAE) was prepared by a traditional method. D-mannitol and adipic acid in a molar ratio of 2:1 were added into a mixer set and stirred for 5 min. Then, the mixture was put into a 500 mL three-necked round bottom flask with a mechanical stirring and reflux water device, followed by introducing cyclohexane as the dehydrant. The mixture was heated to 160 ± 1 °C for 3 h, to remove the excess cyclohexane with a vacuum pump. The DMAE was then obtained.

2.2.3 Preparation of di-mannitol adipate ester-based zinc metal alkoxide (DMAE-Zn)

DMAE-Zn was synthesized through the method of alcoholysis. Zinc acetate and DMAE in a molar ratio of 1:1 were mixed in a three-necked flask with a mechanical stirring. Excess absolute ethanol was added and the reactor was then heated to 160 ± 1 °C for 4 h. After the solvent was evaporated, the samples were washed with ethanol for three times to obtain the products, DMAE-Zn.

2.3. Material characterization

Samples were characterized by Fourier transform infrared (FT-IR) spectroscopy (Nicolet 5700) with the KBr disc method. Spectral range was 400-4000 cm^{-1}, with a scan rate 128 min^{-1} and a resolution of 4 cm^{-1}. The blank spectrum was tested before each measurement to eliminate the spectrum subtraction resulting from carbon dioxide and water in the air. TGA and DTG of the samples were performed using a Q500 analyzer (TA instruments, United States) at a 10 °C min^{-1} heating rate from 25 to 700 °C in nitrogen atmosphere. The results were used to investigate the decomposition of the materials [26].

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2.4. PVC sample preparation

About 100.0 g of PVC, 5 mL of dioctyl phthalate (DOP), 4.0 g of TiO_2, 9.0 g of chlorinated polyethylene (CPE), 2.0 g of acrylics copolymer (ACR), 20.0 g of $CaCO_3$, 1.6 g of stearic acid and 4 g of thermal stabilizers were added into a blender to undergo sufficient mixing. Then the mixture was milled using an open twin-roller (PX-GY-150, Shenzhen Pengxiang Yunda Machinery Technology Co., China) at 180 ºC for 5 min to produce the PVC sheets with a thickness of about 1.0 mm.

2.5. Thermal stability test

2.5.1. Conductivity measurement

PVC sheets were cut into small square pieces of 0.5 mm × 0.5 mm with a total weight of 2.0 g, and put into a home-made reaction vessel. The vessel was placed in an oil bath and heated to 180 ºC. Then 60 mL of deionized water was added in a beaker of 100 mL for testing its conductivity. The HCl gas produced during the thermal decomposition of PVC was introduced into the measuring beaker by the nitrogen stream (about 7 L/h). The HCl was absorbed by the deionized water in the measuring beaker so that the conductivity of water gradually changed with time. Therefore, the decomposition rate of PVC can be recorded through measuring the change of the conductivity of the deionized water. A conductivity meter (DDS-307, Shanghai Instrument Electric Scientific Instrument Co., Ltd) was used to measure the conductivity.

2.5.2. Thermal aging test

PVC sheets were cut into small samples of 15 mm × 15 mm size. These sheets were heated to 180 ºC in an oven. The sheets were taken out after every 10 minutes. The thermal stability of PVC was evaluated by monitoring the color change.

2.5.3. UV-VIS spectroscopy test

It is known that PVC begins to decompose and produce conjugated double bonds when the temperature reaches 130 ºC. PVC samples were first dissolved by tetrahydrofuran (THF). Then the concentration of conjugated double bonds was measured by UV-visible spectrometer (UV-VIS). The UV-VIS spectra were recorded

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at 25± 5 °C by using a UV-2450PC spectrometer with the slit width set at 2 nm over the wavelength range of 200-500 nm.

2.5.4 Torque rheometer test

The effect of DMAE-Zn on the dynamic rheological properties of PVC was tested by a torque rheometer (RM-200C, Harbin Harp Electric Technology Co.). Operating temperature was set at 180 °C while keeping the rotor with a speed of 35 rpm.

2.5.5. The capacity for neutralizing HCl

The capacity of stabilizers to neutralize HCl was investigated byh conductometric titration experiments. 6.00 mL of 0.1 M HCl standard solution was diluted with 20.00 mL of ethanol and 10.00 mL of deionized water. 0.0500 g of thermal stabilizer, such as DMAE-Zn, lead salts, $ZnSt_2$, $CaSt_2$, and so on was dissolved in this solution with a magnetic stirring at 40 °C. The excess HCl was back-titration with 6.00 mL of 0.1 M NaOH standard solution. The conductivity of the solution was measured by a conductivity meter (DDS-307, same as 2.5.1.). The volume of NaOH solution corresponding to the minimum conductivity of the solution was the titration endpoint, and the capacity for neutralizing HCl was calculated by the volume of NaOH solution used.

3. Results and discussion

3.1. Characterization of metal alkoxides

3.1.1. Fourier Transform Infrared spectroscopy

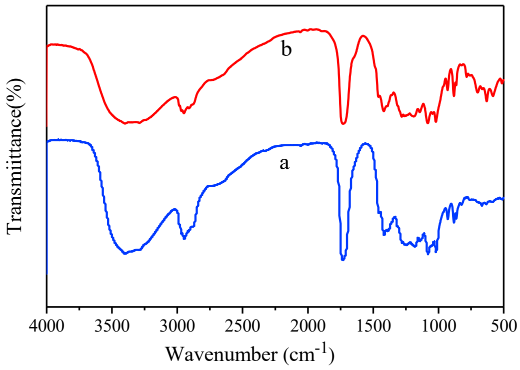

Fig. 1 FT-IR spectra of the raw material and product: (a) DMAE; (b) DMAE-Zn.

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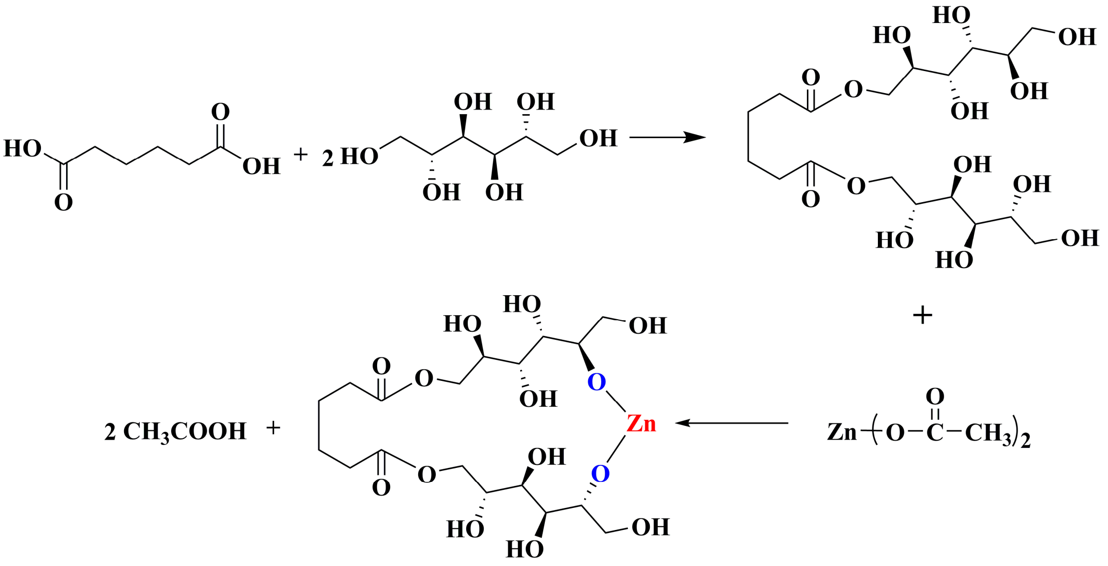
Fig. 1 is the FT-IR spectra of the synthesized DMAE and DMAE-Zn. Fig. 1 shows that both the DMAE and DMAE-Zn have strong peaks at 3400-3500 cm^{-1} which are the characteristic absorbance band of –OH, as a result of the stretching vibration. The peak at about 2900 cm^{-1} was the stretching vibration of the –C-H groups. The absorption peak at about 1738 cm^{-1} can be assigned to the ester carbonyl bonds (-C=O). There were no absorption peaks at 1786 cm^{-1} of carboxylic acid carbonyl bonds in DMAE and DMAE-Zn, indicating that the esterification of stearic acid with D-mannitol was complete. The absorption bands between 650-550 cm^{-1} in Fig. 1b were attributed to the -O-Zn bonds [24]. The appearance of -O-Zn bands indicated that the synthesized compound contained metal alkoxides.

There are six hydroxyl groups in a D-mannitol molecule. All of these hydroxyl groups can be esterified using adipic acid. Therefore, DMAE may contain more than twelve esters. Its derivative, DMAE-Zn is expected to have a more complex structure. **Scheme 1** shows a simplified reaction pathway for the synthesis of DMAE-Zn. Two carboxyl groups of adipic acid react with two alcohols hydroxy of the di-mannitol to form esters. Then, through alcoholysis reaction, the ethyoxyl of ethanol zinc will exchange with the hydroxy of polyol ester. After completely evaporating the ethanol, the targeted DMAE-Zn can be obtained.



Scheme 1. Synthesis pathways of DMAE-Zn

3.1.3. Thermogravimetric analysis

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Fig. 2 shows the TGA, DTA and DTG curves of the targeted DMAE-Zn. There was one weight-loss step within the temperature range from 200 to 500 °C in the TG curve of the DMAE-Zn, which was accompanied by a maximum weight-loss peak. The DTG curve of Fig. 2 shows that there are two pyrolysis temperatures for DMAE-Zn, 265.8 and 342.5 °C, respectively. All the pyrolytic temperatures were far more than 180 °C which is the processing temperature of PVC, meaning that the synthesized DMAE-Zn did not break down during PVC processing and suitable to be used as thermal stabilizers of PVC. TG curve in Fig. 2 shows that the residue is 20.57%, which is slightly higher than the result of elemental analysis. The residue might be composed of ZnO and carbon. DTA curve in Fig. 2 shows that the melting point of the targeted DMAE-Zn can be estimated from the first endothermic peak where the weight changes slightly. Thus, the melting point of DMAE-Zn can be estimated to be 154.4 °C, lower than PVC processing temperature (180 °C). Therefore, the targeted metal alkoxides had a good compatibility with PVC.

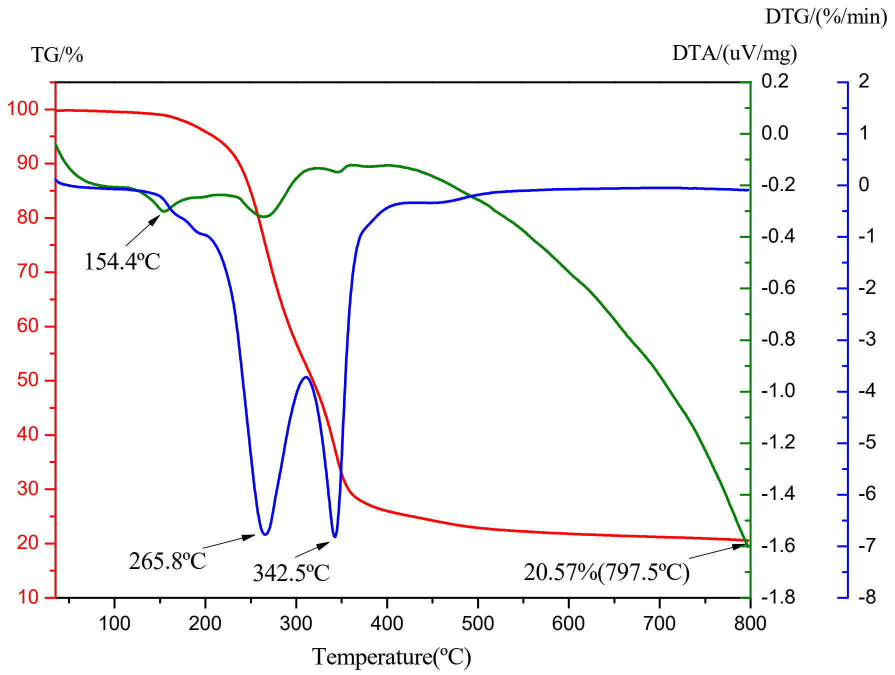

Fig. 2 TGA, DTA, and DTG curves of the targeted DMAE-Zn

3.2. Thermal stability tests of DMAE-Zn on PVC

3.2.1 Conductivity test

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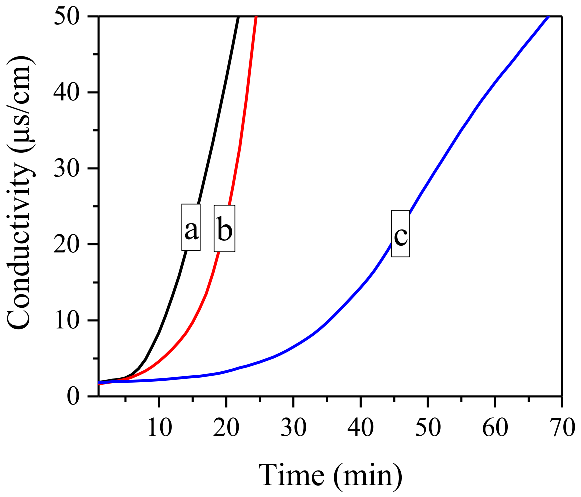

Fig.3 Conductivity versus time plots for (a) pure PVC; and PVC stabilized by 4 phr of (b) $CaSt_2/ZnSt_2$ (1:1); (c) DMAE-Zn

In the tests, nitrogen gas, as a carrier gas, carries HCl gas released during the degradation of PVC into the deionized water. The dissolution of HCl into the deionized water will change the conductivity of the water. As a result, the degradation rate of PVC can be estimated by testing the rate of change in the conductivity of the water. In the Conductivity vs. Time plot, the introduction time (T_i) refers to the time from the start of the heating to when the conductivity starts to rise, while the stability time (T_s) refers to the time where the conductivity of the water reaches 50 μS cm^{-1} [30], which can be considered as the maximum acceptable conductivity value in PVC degradation.

Fig. 3 is the Conductivity vs. Time plots for pure PVC and PVC stabilized by 4 phr of $ZnSt_2/CaSt_2$ (1:1), and DMAE-Zn, respectively. Generally speaking, the shorter the T_i, the worse the color stability of PVC. It can be seen from Fig. 3 that the T_i and Ts of pure PVC are 9.6 min and 21.8 min, respectively, indicating that the initial color stability of pure PVC is quite short and, after having been heated for 21.8 min, pure PVC might degrade completely. As for the PVC samples stabilized by $ZnSt_2/CaSt_2$, Fig. 3b shows that the T_i and T_s of PVC stabilized by $ZnSt_2/CaSt_2$ are 16.1 min and 24.3 min, respectively. By comparing Fig. 3a and Fig. 3b, although the T_i of PVC stabilized by $ZnSt_2/CaSt_2$ is longer than that of pure PVC, the T_s values of these two PVC samples are relatively close. This means that the initial stability of PVC stabilized with $ZnSt_2/CaSt_2$ was better than that of pure PVC. However, the long-term stability of PVC stabilized with ZnSt$_2$/CaSt$_2$ was worse. This is because that ZnCl$_2$ would be produced when ZnSt$_2$ absorbed HCl produced during PVC degradation. ZnCl$_2$ was a strong Lewis acid, which would catalyze the degradation of the PVC. When the amount of ZnCl$_2$ was accumulated to a certain extent, it would suddenly accelerate the degradation of PVC, leading to rapid aging of PVC. This phenomenon was called “zinc-burning” [31]. It was worth noting that the T_i and T_s of PVC stabilized by DMAE-Zn was extended to 31.1 min and 67.9 min, respectively, indicating this PVC samples had an excellent color stability and long-term stability. This might be due to the fact that DMAE-Zn had many hydroxyl groups, which might complex with the produced ZnCl$_2$ to inhibit the catalytic degradation of PVC.

3.2.2 The thermal aging test

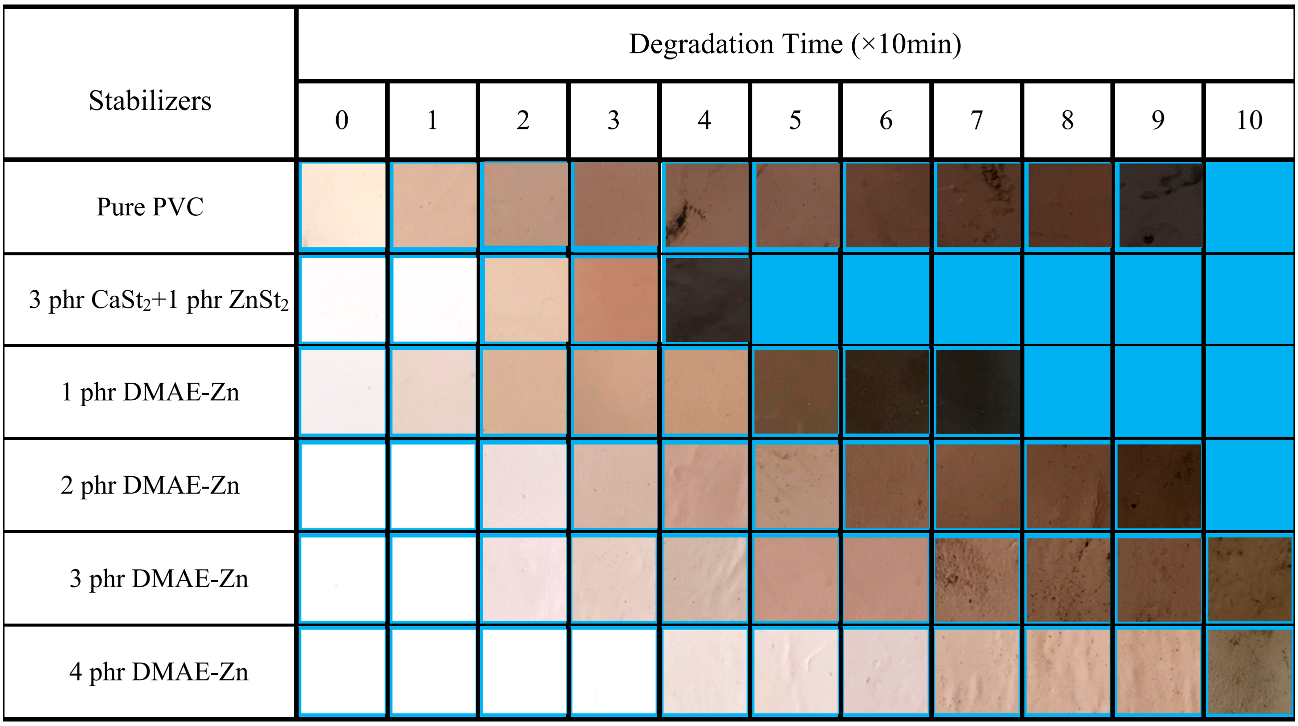

Fig.4 Color evolution of PVC samples with different thermal stabilizers at 180°C

When the temperature exceeds 120 °C, PVC starts thermal degradation. The unstable chlorine atoms, such as allyl chloride and tert-butyl chloride, would combine with hydrogen atoms in the ortho to form hydrogen chloride, and the -C=C- comes into being. Further thermal degradation will produce a double bond of the conjugated structure. When the conjugated structure increases to a certain length, the color of PVC will change into light brown, and then dark brown, finally turn black.

Fig. 4 shows the thermal aging test results of pure PVC and PVC with 4 phr of $ZnSt_2/CaSt_2$ (1:3), and 1 to 4 phr of DDMA. The initial color (heated for 0 min) of pure PVC is light yellowish gray, indicating that slight thermal degradation occurs during the preparation of pure PVC sheets with the two-roll tablet press. As the heating time increases, the color of pure PVC gradually changed into light brown (after 10 min), brown (after 30 min), and black (after 90 min). PVC samples stabilized by $ZnSt_2/CaSt_2$ (1:3) had an excellent initial color, showing that the formula of $ZnSt_2/CaSt_2$ can improve the initial color of PVC. It is worth noting from Fig. 4 that, after having been heated for 40 min, the color of PVC stabilized by $ZnSt_2/CaSt_2$ turned dark brown quickly, indicating the “zinc-burning” phenomenon and a poor long-term thermal stability of the formula of $ZnSt_2/CaSt_2$ for PVC.

It can be seen from Fig. 4 that the initial color of PVC sheets with 1 phr of DMAE-Zn is white and changes slowly into pale yellow brown and brown within 40 min, indicating that the addition of DMAE-Zn can improve the color stability of PVC. However, from 50 min, the color of the PVC stabilized by 1 phr of DMAE-Zn turned dark brown quickly within 10 min, showing that 1 phr of DMAE-Zn was not enough to improve the long-term thermal stability of PVC. Fig. 4 proves that as the dosage of DMAE-Zn increased, the color of PVC can be improved significantly. It can be also seen from Fig. 4 that the thermal stability of PVC stabilized by 2 phr and 3 phr of DMAE-Zn has the similar efficiency. PVC stabilized with 4 phr of DMAE-Zn has the best initial color and, the color starts slowly turning yellow from 60 min and does not turn to completely back within 120 min, showing that 4 phr of DMAE-Zn has the highest thermal stabilizing efficiency.

3.2.3. UV-VIS spectroscopy test

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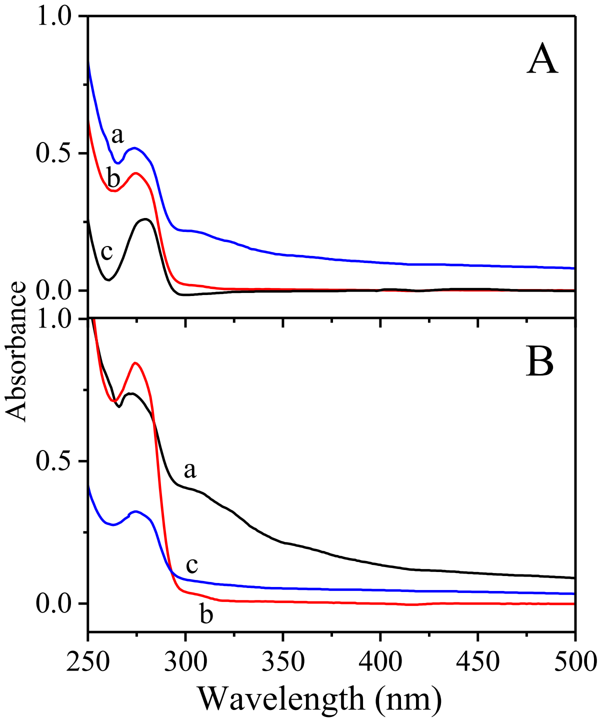

Fig. 5 UV-VIS spectrum of pure PVC and PVC stabilized with different thermal stabilities heated for 0 min (A) and 60 min (B) at 180 ºC. a: Pure PVC; b: $CaSt_2/ZnSt_2$; c: DMAE-Zn

When the PVC is thermally degraded, a conjugated double bond structure is produced. The conjugated double bond structure has a distinct absorption peak in the UV-VIS spectrum. Furthermore, the length of the conjugated double bond affects the position of the absorption peak, and the greater the concentration of the double bond (C_{db}), the higher the absorption peak. Fig. 5 reveals the UV-VIS spectra of pure PVC and PVC stabilized by 4 phr of different thermal stabilizers which are heated for 0 min (A) and 60 min (B) at 180 ºC. The maximum absorption peak of three samples is at about 280 nm which belongs to the conjugated triene structure formed in the dehydrochlorination of PVC. Pure PVC exhibited the highest C_{db}, indicating that $CaSt_2/ZnSt_2$ and the targeted metal alkoxides were effective to improve the initial thermal stability of PVC. Between the two thermal stabilizers, the peak height of PVC stabilized with $CaSt_2/ZnSt_2$ was the higher one, suggesting that the formula with a ratio of $CaSt_2$ to $ZnSt_2$ of 3 was not effective to improve the initial color of PVC, probably because of less $ZnSt_2$ and more $CaSt_2$ ($ZnSt_2$ is the best additive in

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improving initial color of PVC). As for the targeted DMAE-Zn, Fig. 5A shows that the peak height of PVC stabilized by DMAE-Zn is the lowest, indicating the lowest C_{db} in PVC stabilized by DMAE-Zn . These results confirmed that DDMA is most efficient in improving the thermal stability of PVC, consistent with the results of the oven thermal aging tests.

Compared with Fig. 5A, the C_{db} of PVC samples in Fig. 5B increase greatly. Especially, after having been heated for 60 min, the C_{db} of PVC stabilized with $CaSt_2/ZnSt_2$ became the biggest one, even exceeded that of pure PVC. It was because that “zinc-burning” phenomenon happened in PVC stabilized by $CaSt_2/ZnSt_2$. The results of oven thermal aging tests (Fig. 4) also confirmed this conclusion, in which the color of PVC sheet $CaSt_2/ZnSt_2$ already became dark gray after being heated for 60 min. The C_{db} of PVC stabilized by the synthesized DMAE-Zn did not increase evidently, just increased from 0.26 to 0.32, indicating that DMAE-Zn had the highest efficiency in suppressing the production of conjugated double bonds.

The position of absorption peaks should also be noted. Compared Fig. 5 A and B, it can be seen that the position of these main absorption peaks do not shift, showing that most of the PVC thermal degradation products are the conjugated triene structure. However, the absorbance curve of pure PVC (see Fig. 5Aa) shows that there is weak absorption at the range of 300-330 nm which belongs to tetraenes and pentaene. PVC samples stabilized by the two thermal stabilizers have no absorption at the same range. Fig. 5B shows that, after having been heated for 60 min, the absorbance curve of pure PVC increased obviously at the range of 300-330 nm. This suggests that the C_{db} of tetraenes and pentaene in pure PVC has further increased. The absorbance curve of PVC stabilized by DMAE-Zn increased slightly at the range of 300-330 nm. What’s surprising was that the absorbance curve of PVC stabilized by $CaSt_2/ZnSt_2$ still did not increase, indicating that $ZnCl_2$ produced from the reaction between $ZnSt_2$ and HCl intends to catalyze the PVC degradation to only form conjugated triene.

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3.2.4. Synergy between DMAE-Zn and $CaSt_2$ or $ZnSt_2$ on PVC thermal stability

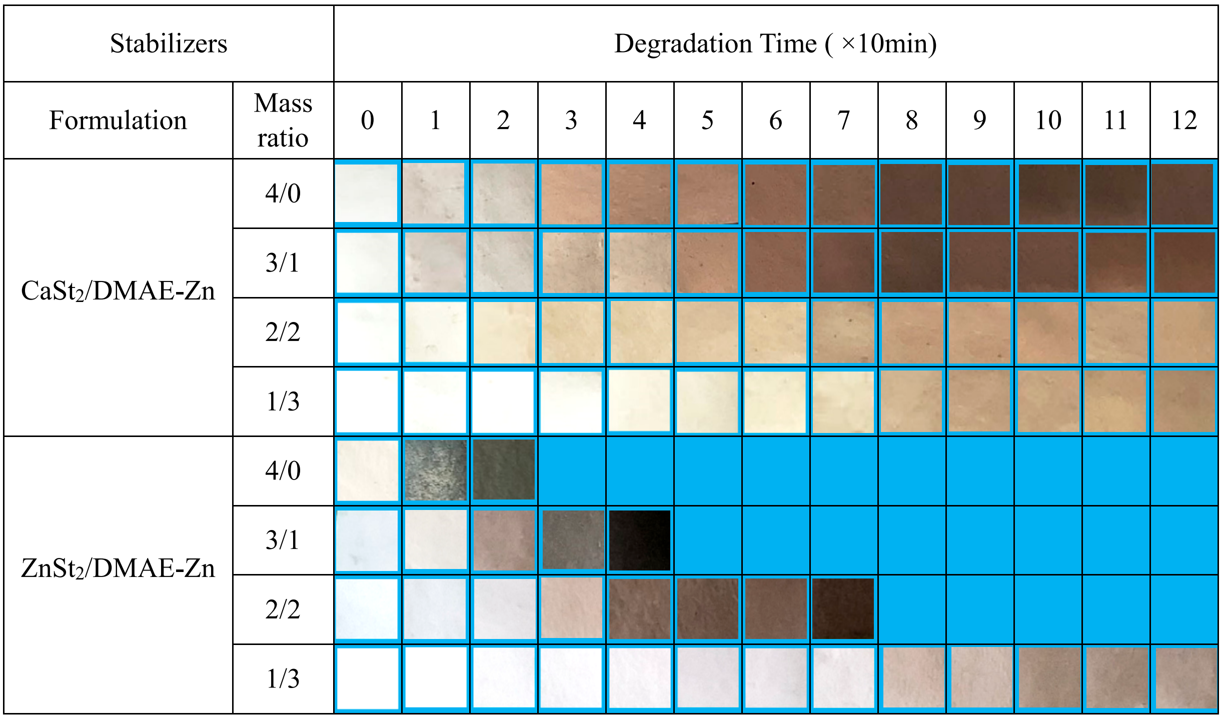

Fig. 6 Oven thermal aging test results of PVC stabilized by $CaSt_2$/DMAE-Zn and $ZnSt_2$/DMAE-Zn

The above results (Section 3.2.1 - 3.2.3) indicated that DMAE-Zn is an efficient c thermal stabilizer for PVC. In order to improve PVC color thermal stability and reduce manufacturing cost (if it can be industrialized), the synergistic effect of DMAE-Zn with $CaSt_2$ and $ZnSt_2$ on PVC thermal stability was investigated. Fig. 6 shows the oven thermal aging test results of PVC stabilized by $CaSt_2$/DMAE-Zn and $ZnSt_2$/DMAE-Zn, respectively. It can be seen from that the color of PVC stabilized by 4 phr of $CaSt_2$ starts to turn light brown after being heated 10 min, and turns darken brown at 60 min, showing that pure $CaSt_2$ cannot improve the PVC thermal stability significantly. The color of PVC with 3 phr of $CaSt_2$ + 1 phr of DMAE-Zn turns into black at 60 min, indicating that the thermal stability of this formula is similar with that of pure $CaSt_2$. With increasing DMAE-Zn, the thermal stability of PVC was improved quickly. For example, the color of PVC stabilized by $CaSt_2$/DMAE-Zn with the mass ratio of 2:2 and 1:3 did not turn black until 120 min. Especially, the color of PVC stabilized by $CaSt_2$/DMAE-Zn with mass ration of 1:3 did not change within 30 min,

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and only turned slight brown within the next 40 min, indicating that there existed a good synergistic effect between $CaSt_2$ and DMAE-Zn on PVC thermal stability.

As for the system of $ZnSt_2$/DMAE-Zn, Fig. 6 shows that, when the $ZnSt_2$ is used alone as a PVC thermal stabilizer, PVC samples turn black quickly within 10 min due to the "zinc-burning" phenomenon. With the dosage of DMAE-Zn increasing, the initial color and long-term stability of PVC can be improved obviously. For example, color of PVC stabilized by $ZnSt_2$/DMAE-Zn with the mass ratio of 1:3 remained unchanged in 70 min, and did not turned black in 120 min. Therefore, there existed excellent synergistic effect between $ZnSt_2$ and DMAE-Zn on PVC thermal stability. It was probably because that there were a large number of hydroxyl groups in DMAE-Zn which could complex with $ZnCl_2$ to avoid catalyzing PVC thermal degradation.

3.2.5. Torque rheology test of DMAE-Zn

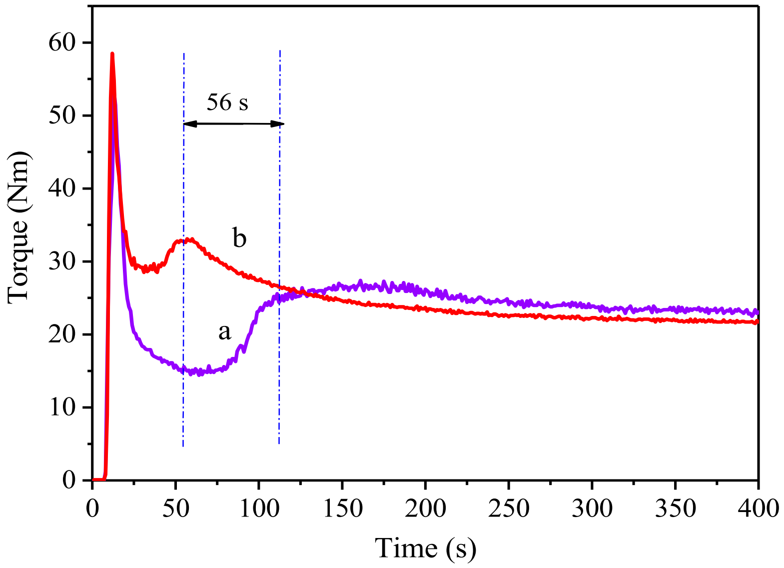

Fig. 7 Torque rheology test results obtained at 180 °C on pure PVC (a) and PVC stabilized by DMAE-Zn (b)

The torque rheology test was according to ASTM D 2538-02 [32], operated at 180 °C as was described in **Section 2.6.4**. Fig. 7 shows the results for pure PVC and PVC stabilized by DMAE-Zn. Both samples had two distinct peaks which were the feed peak and plasticized peak of PVC resin, respectively. The first peaks for both samples come out at almost the same time. The first peak height of PVC stabilized by DMAE-Zn was 50 Nm higher than that of pure PVC, indicating that the addition of DMAE-

Zn did not improve the lubricating property of PVC. The second peaks of pure PVC and PVC stabilized by DMAE-Zn however appeared at different time points. Pure PVC required approximately 111 s to complete the plasticization. In PVC stabilized by DMAE-Zn case, however, plasticization was completed in 55 s. The significantly reduced plasticizing time obtained by incorporating DMAE-Zn as compared to pure PVC confirmed the excellent plasticizing effect of DMAE-Zn on PVC. It is well known that plasticizers must have a good compatibility with PVC. For example, Gilbert et al. reported that plasticizers acted as solvents for amorphous regions of PVC, and the PVC chains in the amorphous regions might become solvated at elevated temperatures during processing [33]. Therefore, we can draw such a conclusion that the reason why DMAE-Zn had a good plasticizing effect on PVC is that DMAE-Zn has a good compatibility with PVC chains in the amorphous regions. It is also worth noting that the balance torque of PVC stabilized by DMAE-Zn was slightly lower than that of pure PVC. Considering that DMAE-Zn had no lubricity to PVC, lower balance torque of PVC stabilized by DMAE-Zn indicated that the addition of DMAE-Zn could decrease friction between PVC molecules through solvation.

3.3. The thermal stabilizing mechanism of DMAE-Zn

In our previous work, we found that, due to its high electronegativity, the alkyl oxygen of metal alkoxides had a tendency to attack the carbon atoms (given its high positive charge) attached to allyl chloride in PVC chains **[15]**. At the same time, allyl chloride with a high electronegativity would attack the zinc atom (having high positive charge) of the metal alkoxides. **Scheme 2** illustrates the reaction mechanism. This reaction mechanism also applies to DMAE-Zn since it contains metal alkoxides, which could explain the fact that PVC stabilized by DMAE-Zn had a better initial color (i.e., white) than pure PVC (Refer to **Fig. 4**). The allyl chloride in PVC formed bonding with the Zn atom in DMAE-Zn. The released Cl atoms from PVC were taken up by zinc ions in DMAE-Zn (**Scheme 2a**) and generate compound I, which prevents the formation of free $ZnCl_2$. This explains the excellent long-term thermal stability observed for PVC stabilized by DMAE-Zn (**Fig. 4**).

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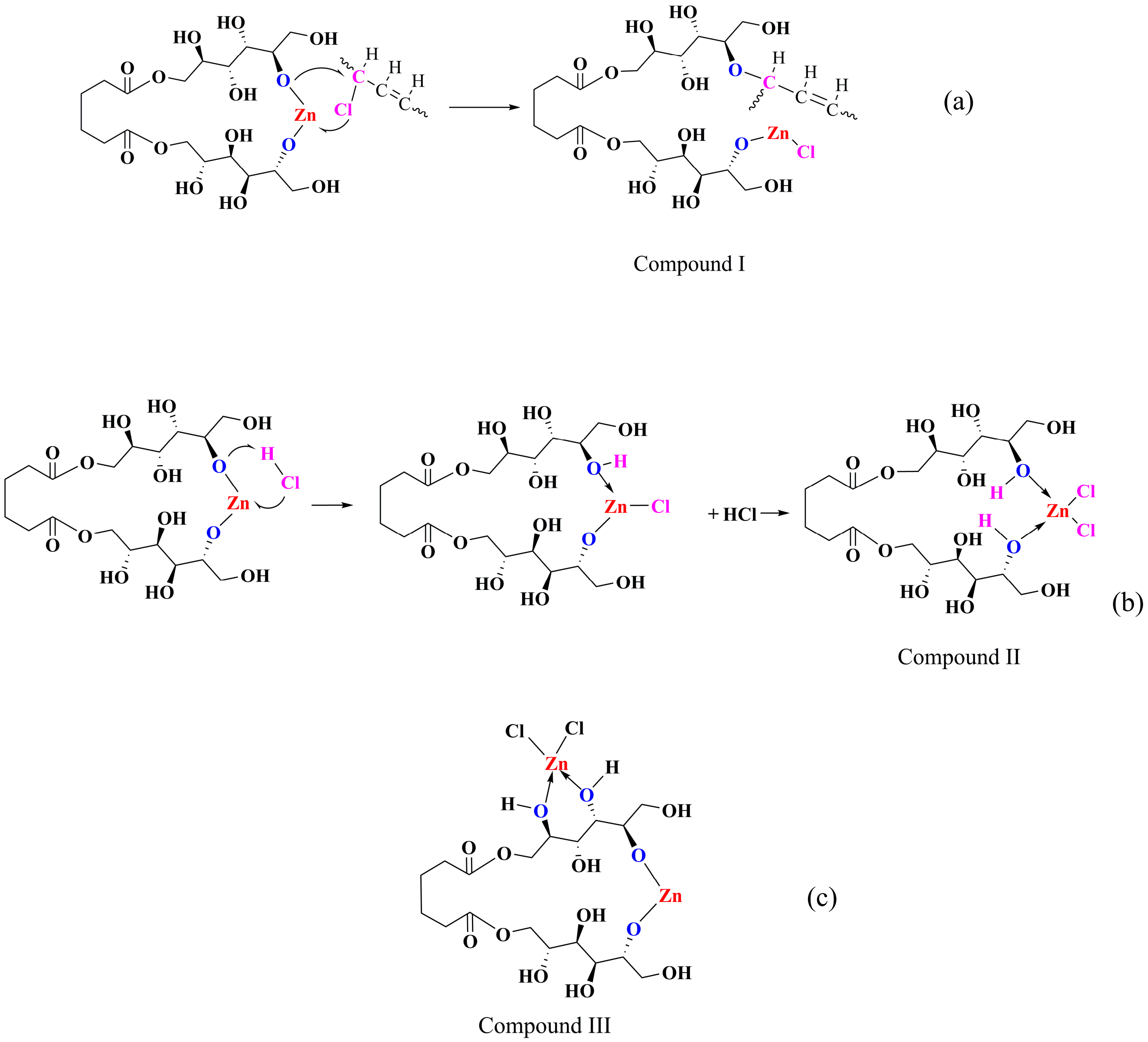

Scheme 2. The schematic diagram of DMAE-Zn to replace allyl chloride (a), to neutralize HCl (b), and to complex $ZnCl_2$ (c)

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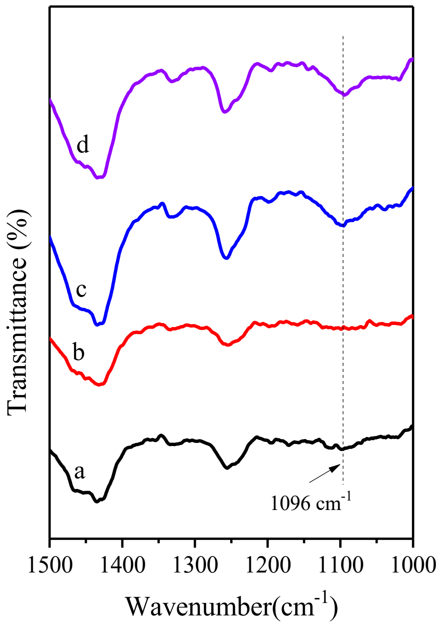

Fig. 8 FTIR results of pure PVC and PVC stabilized by DMAE-Zn heated at 180 ºC. Pure PVC heated for 0 min (a) or for 30 min (b); PVC stabilized by DMAE-Zn heated for 0 min (c) or for 30 min (d).

In order to verify this mechanism of DMAE-Zn, FTIR spectra were used to test pure PVC sheets and PVC sheets stabilized by DMAE-Zn heated at 180 ºC for 0 min and 30 min. Fig. 8 shows the FTIR results. The obvious absorption peaks at 1096 cm^{-1} in curve c and d are the characteristic peaks corresponding to -C-O-C-, improving the feasibility of mechanism that the alkyl oxygen of metal alkoxides attacks the carbon atom attached to allyl chloride (showing in **Scheme 2a**). There was no characteristic absorption peaks at 1096 cm^{-1} in curve a and b.

Table 2 The HCl absorption capacity of different thermal stabilizers for PVC

Stabilizer	HCl absorption capacity, mg (HCl) / g (stabilizer)
Lead salts	280.1
$ZnSt_2$	98.2
$CaSt_2$	87.6
DMAE-Zn	131.4

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Conductivity titration experiment was carried out to verify the ability of DMAE-Zn to absorb HCl. The experimental method was described in **Section 2.5.5**. The results are shown in Table 2. Table 2 shows that lead salts has the highest capacity to absorb HCl, reaching 281.1 mg/g. HCl absorption capacity of DMAE-Zn was 131.4 mg/g, which was larger than that of $ZnSt_2$ and $CaSt_2$, showing that DMAE-Zn could improve the long-term thermal stability of PVC.

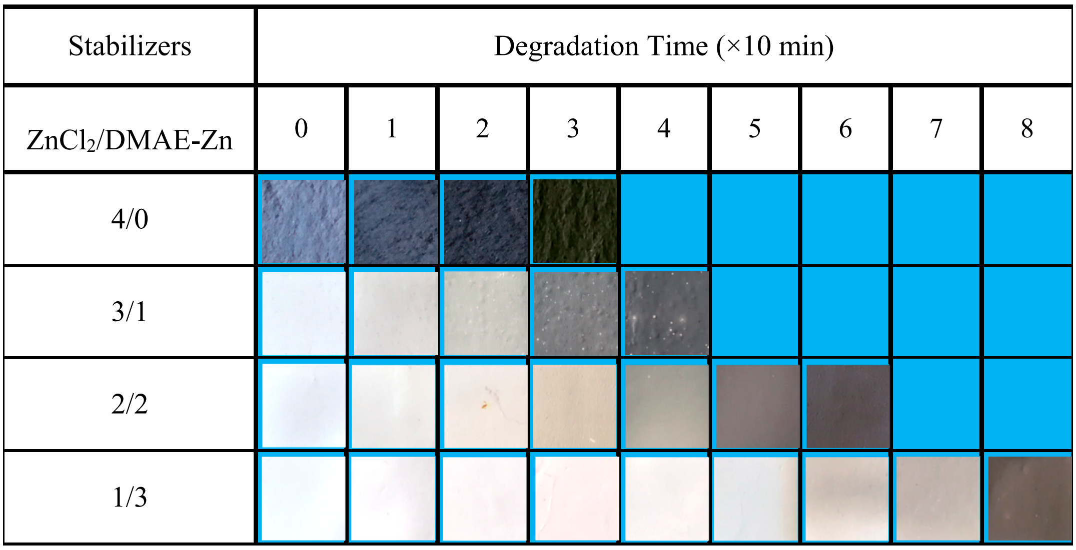

Fig. 9 Color evolution of PVC samples with different ratio of $ZnCl_2$ and DMAE-Zn heated at 180 °C for different time

In general, the addition of an auxiliary thermal stability is very important if a zinc atom is present in the thermal stability due to the "zinc-burning" phenomenon. It can been seen from Fig. 4 that there is no "zinc-burning" phenomenon on PVC samples stabilized with pure DMAE-Zn. Furthermore, PVC sample stabilized by 3 phr of DMAE-Zn + 1 phr of $ZnSt_2$ also has a good long-term thermal stability. All the results indicate that the $ZnCl_2$ produced during the replacement of the active chlorine atom or the neutralization of HCl can be chelated by –OH of DMAE-Zn in situ (illustrated in **Scheme 2b** and **c**, and generate compound II and III). In order to verify the complexation of DMAE-Zn with $ZnCl_2$, oven thermal aging experiments were conducted to test the thermal stability of PVC samples stabilized by 4 phr of pure $ZnCl_2$, and 4 phr of different proportions of $ZnCl_2$/DMAE-Zn mixtures. The results are shown in Fig. 9. PVC samples containing 4 phr $ZnCl_2$ is quickly darken in 10 min. It demonstrated that $ZnCl_2$ accelerated the thermal degradation of PVC, meaning that

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"zinc-burning" phenomenon happened. With the increase of the ratio of DMAE-Zn, the initial color and long-term stability of PVC stabilized by $ZnCl_2$/DMAE-Zn mixture can be improved. Especially, the PVC samples with 1 phr of $ZnCl_2$ + 3 phr of DMAE-Zn have the excellent thermal stability, as shown in Fig. 9 that the initial color did not change within 50 min and became black completely after heated for 70 min. At the end, the PVC samples with 1 phr of $ZnCl_2$ + 3 phr of DMAE-Zn also happened "zinc-burning" phenomenon, because it would exceed the ability of DMAE-Zn to chelate $ZnCl_2$.

4. Conclusions

In this study, DMAE-Zn was synthesized through alcoholysis reaction. The chemical formations were confirmed through FT-IR; The thermal stability on PVC was studied using thermal aging tests, onductivity test, UV-VIS spectroscopy test, and torque rheology test. The results showed that PVC stabilized by DMAE-Zn had a good initial color and long-term stability, and good plasticizing performance. Moreover, the results of oven thermal aging experiments indicated that there were a good synergy between DMAE-Zn, $CaSt_2$ and $ZnSt_2$ in improving the thermal stability of PVC. Furthermore, the thermal stabilizing mechanism of DMAE-Zn on PVC was also studied through the FT-IR, HCl absorption capacity test, compound experiments with $ZnSt_2$. The results confirmed that DMAE-Zn have the common character of metal alkoxides, which would readily neutralize HCl. FT-IR showed that it was the alkoxy group of DMAE-Zn to replace the unstable chlorine atoms on PVC chains to improve the initial color thermal stability of PVC. HCl absorption capacity of DMAE-Zn (131.4 mg/g) was larger than that of $ZnSt_2$ and $CaSt_2$, indicating that DMAE-Zn can improve the long-term thermal stability of PVC. It was also found that there were plenty of hydroxy on DMAE-Zn which could complex $ZnCl_2$ to delay or avoid "zinc-buring" phenomenon.

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