

INFLUENCE OF LANTHANUM STEARATE AND CALCIUM/ZINC STABILIZERS ON STABILIZATION EFFICIENCY OF DIBUTYLTIN DILAURATE TO POLYVINYL CHLORIDE*

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Abstract Influences of lanthanum stearate (LaSt_3) and calcium stearate/zinc stearate (Ca/Zn) stabilizers on stabilization efficiency of dibutyltin dilaurate (DBTDL) to polyvinyl chloride (PVC) in air were investigated. The results revealed that the stabilization effect of DBTDL could be achieved by the La/Sn stabilizers with a ratio of 8/2. Addition of DBTDL could enhance thermal property and reduce dynamic storage modulus (G') at 180°C for PVC containing LaSt_3 or Ca/Zn stabilizers. On the other hand, incorporation of LaSt_3 did not influence the stabilization efficiency of DBTDL markedly; while addition of Ca/Zn stabilizers could significantly decrease thermal property for the DBTDL stabilized PVC. Furthermore, the effects of LaSt_3 and Ca/Zn stabilizers on the stabilization efficiency of DBTDL were explained in the framework of ionization potential.

Keywords: Polyvinyl chloride (PVC); Calcium/zinc stabilizers; Lanthanum stearate; Dibutyltin dilaurate; Ionization potential.

INTRODUCTION

Polyvinyl chloride (PVC) has played a key role in the development of plastics industry due to the excellent mechanical, insulation and flame retardant properties^[1]. However, the poor thermal and photochemical stability limits the processibility and application of PVC products^[2]. The thermal instability of PVC is mainly caused by abnormal structures such as allylic chloride and tertiary chloride structures in the molecular chain^[2–4]. Coloration of PVC advances during thermal processing and light irradiation due to the formation of long polyene chains through the zipper-like dehydrochlorination^[5–7]. Therefore, proper thermal stabilizers must be incorporated into PVC in order to restrain its degradation during thermal processing.

Organotin stabilizers have been widely used because of their strong stabilization effect and good compatibility with PVC^[8]. Researches concerning the influence of organotin groups^[9] and the introduction of halogen^[10] on the stabilization efficiency of organotin stabilizers were reported. Thermal degradation of organotin stabilizers in PVC was investigated by using ^{119}Sn Mossbauer spectra^[11–13]. The stabilization effect of organotin stabilizers is related to many reactions: (1) substitution of activated hydrogen in PVC by the stabilizer molecule or its by-products^[14]; (2) substitution of labile chlorine atoms in PVC by the stabilizer molecule^[15–17]; (3) saturation of the degraded PVC by by-products of the stabilizer or hydrogen chloride (HCl)^[18–20]. Organotin stabilizers might react with PVC only through structural defects rather than the normal structures^[17], leading to

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alteration of the sequence length and distribution of polyene sequences^[21, 22].

Ca/Zn stabilizers have been used widely due to the synergistic effect and favorable stabilization effect for PVC^[23–27]. Recently, rare earth compounds such as tris(mono-*i*-octylphthalate)^[28], stearates^[29], citrates^[30] and malates^[30] have been used as thermal stabilizers in PVC because of their excellent long-term stabilization effect. In a previous study, we found that lanthanum stearate (LaSt₃) has a synergistic effect with Ca/Zn stabilizers and the complex stabilizer composed of LaSt₃ and Ca/Zn stabilizers can play an important role in stabilizing PVC^[31].

Because of high cost and toxicity of organotin stabilizers, combination of organotin with other effective nontoxic stabilizers (such as Ca/Zn stabilizers) has attracted researchers' interests recently. Addition of Zn compounds to an organotin recipe shows a moderate positive effect for the initial coloration while a combination of calcium glycolate and organotin chloride is not at all effective for the thermal stabilization of PVC^[32]. For PVC containing both organotin and Ca/Zn stabilizers, organotin conceals the effect of CaSt₂ while ZnSt₂ is more active than organotin in stabilizing PVC^[33]. Explanations of the aforementioned phenomena were not yet reported. It is suggested that some reactions between zinc chloride (ZnCl₂) and organotin happen during the processing and the product organotin chloride is less powerful than ZnCl₂ as a dehydrochlorination catalyst^[32]. A regenerative mechanism to explain the synergistic effect induced by mixtures of alkyltin mercaptoesters as PVC stabilizers has been proposed^[34].

In this article, we aim to study the effects of LaSt₃ and Ca/Zn stabilizers with dibutyltin dilaurate (DBTDL) on thermal, rheological and aging properties of PVC. The stabilization mechanism of DBTDL in combination with LaSt₃ and Ca/Zn stabilizers would be discussed on the basis of infrared spectra and explained in the framework of ionization potential.

EXPERIMENTAL

Materials

PVC (SG5) and ACR (401) were supplied by Hangzhou Chuanhua Co. Ltd., China and Zhiqiang Plastic Aids Plant, China, respectively. Dibutyltin dilaurate (DBTDL) supplied by Shanghai First Medical Plant, China was used as primary stabilizer. Calcium stearate (CaSt₂) from Wenzhou Chemical Reagent Plant, China and zinc stearate (ZnSt₂) from Sinopharm Group Chemical Reagent Co. Ltd., China as well as lanthanum stearate (LaSt₃) from Jiangyin Huashi Plastic Aids Plant, China were used as co-stabilizers.

Samples Preparation

PVC was mixed with 2 phr (per hundred resins) ACR and 3 phr LaSt₃/DBTDL (La/Sn) stabilizers using a Brabender torque rheometer (Brabender, Germany) at 35 r/min and 180°C for 5 min. Another series of samples were made by mixing PVC with 2 phr ACR, 2 phr LaSt₃ or 2 phr CaSt₂/ZnSt₂ (Ca/Zn) stabilizers or 1 phr LaSt₃ plus 1 phr Ca/Zn stabilizers and various amounts of DBTDL (1–4 phr) according to the same procedure. The mixtures were compression-molded at 14.7 MPa and 180°C for 10 min to obtain samples for rheological and aging testing.

Measurements

Fourier transform infrared (FTIR) spectra

FTIR spectra were recorded on a VECTOR 22 spectrometer (Bruker, Germany) with a resolution of 4 cm⁻¹ and a scan-co-addition of 32. A KBr disc was used as a reference to produce a background diffuse reflectance spectrum. The samples were mixed fully in the mortar with KBr and made into discs.

Thermogravimetric analysis (TGA)

Thermal degradation was evaluated on a thermogravimetric analyzer (SDT Q600, TA, USA) from 50°C to 500°C at a heating rate of 20 K min⁻¹ in the condition of air flow.

Rheological testing

Rheological measurements were performed on a Module Advance Rheometric System (MARS, Haake Co.,

USA) using a parallel plate geometry. Frequency (ω) sweep was conducted from 79.85 Hz to 0.07985 Hz at a constant strain of 1% at 180°C.

Aging testing

Aging measurements were carried out on an Electric Blast Drying Oven (101, Shanghai Jinping Instrument Co. Ltd., China) at 180°C, and the samples were withdrawn at predetermined intervals for examining color development.

RESULTS

FTIR Analysis

Figure 1 shows the influence of DBTDL content on FTIR spectra at 3050–2950 cm^{-1} (A) and the relative absorbance of the peak at 3025 cm^{-1} with respect to the peak at 1099 cm^{-1} , A_{3025}/A_{1099} (B), for PVC with and without LaSt₃. The peaks at 3025 cm^{-1} and 1099 cm^{-1} are assigned to the stretching band of C–H in HC=CH and the stretching band of C–C in the main chain of PVC, respectively^[35]. The band at 3025 cm^{-1} is absent for original PVC powder while it appears in all the samples underwent thermal mixing. Addition of DBTDL causes A_{3025}/A_{1099} to decrease for the mixed samples without LaSt₃. On the other hand, addition of LaSt₃ causes an obvious increase in A_{3025}/A_{1099} in comparison with the samples free of LaSt₃.

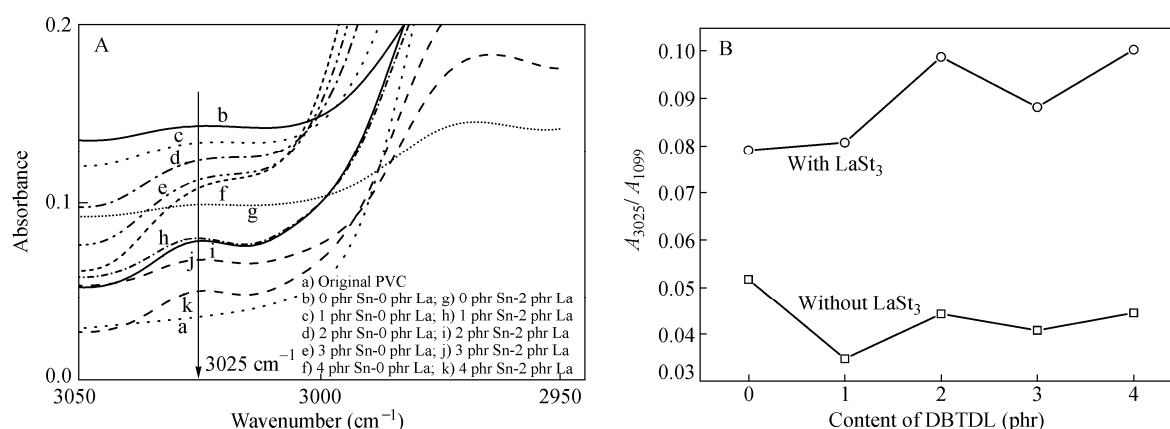


Fig. 1 Influence of DBTDL content on FTIR spectra at 3050–2950 cm^{-1} (A) and relative absorbance A_{3025}/A_{1099} (B) for PVC with and without LaSt₃

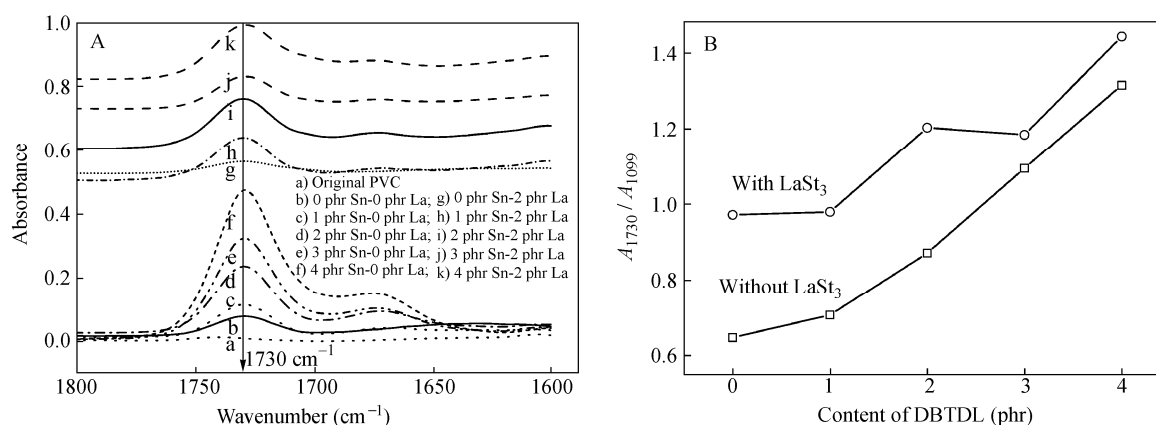


Fig. 2 Influence of DBTDL content on FTIR spectra at 1800–1600 cm^{-1} (A) and relative absorbance A_{1730}/A_{1099} (B) for PVC with and without LaSt₃

Figure 2 presents the influence of DBTDL content on FTIR spectra at $1800\text{--}1600\text{ cm}^{-1}$ (A) and the relative absorbance of the peak at 1730 cm^{-1} with respect to the peak at 1099 cm^{-1} , A_{1730}/A_{1099} (B), for PVC with and without LaSt_3 . The peak at 1730 cm^{-1} is assigned to the stretching band of the $\text{C}=\text{O}$ groups in ACR and the $\text{C}=\text{O}$ groups in DBTDL or LaSt_3 which are substituted to the main chain of PVC^[35]. This is absent for original PVC powder while it appears in all the samples underwent thermal processing. A_{1730}/A_{1099} increases with increasing DBTDL content for thermal processed PVC. Addition of LaSt_3 leads to an increase in A_{1730}/A_{1099} in comparison with the mixed samples without LaSt_3 .

TGA Analysis

Figure 3 demonstrates the influence of La/Sn ratio on the temperature at 5% weight loss, $T_{5\%}$, and the temperature at the maximum rate of weight loss, $T_{\max}$, for PVC containing 3 phr La/Sn stabilizers. Both $T_{5\%}$ and $T_{\max}$ increase markedly with decreasing La/Sn ratio from 10/0 to 8/2. With decreasing La/Sn ratio from 8/2 to 0/10, $T_{5\%}$ remains constant at 280°C while $T_{\max}$ increases slightly.

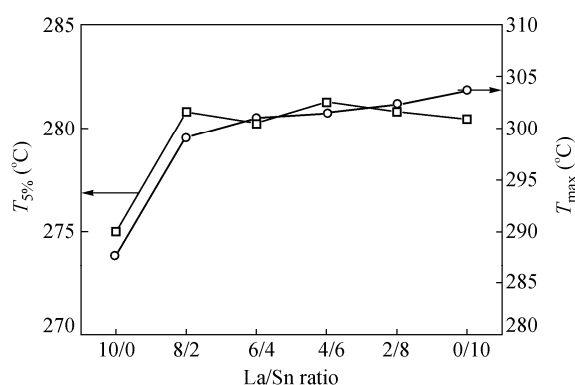


Fig. 3 Influence of La/Sn ratio on $T_{5\%}$ and $T_{\max}$ for PVC containing 3 phr La/Sn stabilizers

Figure 4 shows the influence of DBTDL content on $T_{5\%}$ (a) and $T_{\max}$ (b) for PVC containing different kinds of stabilizers. $T_{5\%}$ increases with addition of 1 phr DBTDL and subsequently decreases at high DBTDL contents for PVC without LaSt_3 and Ca/Zn stabilizers (1) or with 2 phr LaSt_3 (2). Moreover, addition of DBTDL does not influence $T_{5\%}$ markedly for PVC containing 2 phr Ca/Zn stabilizers (3) or 1 phr LaSt_3 plus 1 phr Ca/Zn stabilizers (4). On the other hand, $T_{\max}$ increases gradually with increasing DBTDL content for PVC containing different kinds of stabilizers. In comparison with the DBTDL stabilized PVC, addition of LaSt_3 does not influence $T_{5\%}$ and $T_{\max}$ markedly, while incorporation of Ca/Zn stabilizers results in large decreases in $T_{5\%}$ and $T_{\max}$.

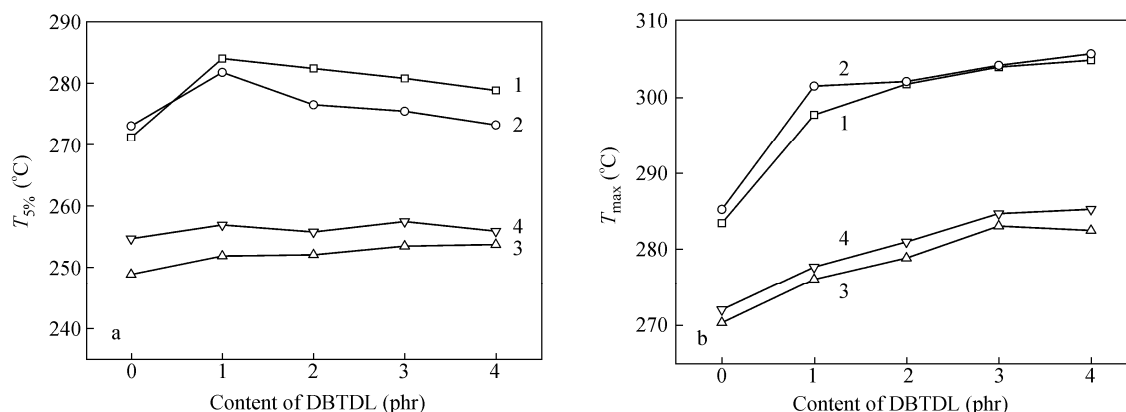


Fig. 4 Influence of DBTDL content on $T_{5\%}$ (a) and $T_{\max}$ (b) for PVC containing different kinds of stabilizers: (1) without LaSt_3 and Ca/Zn stabilizers, (2) 2 phr LaSt_3 , (3) 2 phr Ca/Zn stabilizers, and (4) 1 phr LaSt_3 plus 1 phr Ca/Zn stabilizers

Rheological Behavior

Figure 5 shows the influence of La/Sn ratio on dynamic storage modulus (G') and loss modulus (G'') as a function of ω for PVC containing 3 phr La/Sn stabilizers at 180°C. The sample free of La/Sn stabilizers behaves as a viscoelastic solid as described by $G' > G''$ ^[36–38], $G' \sim \omega^{0.22}$ and $G'' \sim \omega^{0.19}$ in the ω range tested, suggesting the formation of crosslinked structure during thermal mixing and compression molding^[38, 39]. Polyene sequences are formed during thermal degradation of PVC and the released HCl will accelerate the production of polyene sequences, which leads to the formation of crosslinked structure^[2]. Addition of 3 phr LaSt₃ to PVC leads to a slight decrease in G' due to the weak stabilization effect of LaSt₃^[31]. With decreasing La/Sn ratio from 10/0 to 8/2, G' decreases markedly at $\omega < 10$ Hz, which could be ascribed to the strong stabilization effect of DBTDL through restraining the formation of crosslinked structure by altering the sequence length and distribution of polyene sequences^[8, 16, 17]. However, G' remains constant with decreasing La/Sn ratio from 8/2 to 0/10. The variation of La/Sn ratio does not influence G'' markedly.

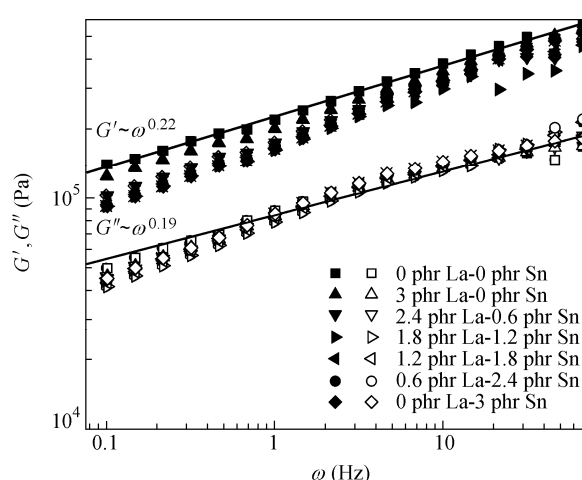


Fig. 5 Influence of La/Sn ratio on dynamic storage modulus (G' , solid symbols) and loss modulus (G'' , hollow symbols) as a function of frequency (ω) for PVC containing 3 phr La/Sn stabilizers at 180°C

Figure 6 demonstrates the influence of DBTDL content on G' as a function of ω for PVC containing different kinds of stabilizers at 180°C. For PVC without LaSt₃ and Ca/Zn stabilizers (a) and for PVC containing 2 phr LaSt₃ (b), G' decreases gradually with increasing DBTDL content. For PVC containing 2 phr Ca/Zn stabilizers (c) or 1 phr LaSt₃ plus 1 phr Ca/Zn stabilizers (d), G' shows a modulus plateau at $\omega < 10$ Hz, revealing that the “zinc burning” phenomena of Ca/Zn stabilizers promote the formation of crosslinked structure^[24]. Moreover, G' decreases obviously with addition of 1 phr DBTDL and then reduces gradually with increasing DBTDL content, revealing that DBTDL can restrain the “zinc burning” phenomena effectively by weakening the autocatalysis effect of the product ZnCl₂ through the reactions with ZnCl₂^[32].

Aging Testing

Figure 7 shows the influence of La/Sn ratio on coloration as a function of the time when the samples were placed in the oven for PVC containing 3 phr La/Sn stabilizers at 180°C. With decreasing La/Sn ratio from 10/0 to 8/2, the initial coloration becomes weak markedly and the color of samples changes from brown to white and transparent. The variation of La/Sn ratio from 8/2 to 0/10 does not influence the initial coloration markedly. The time when the samples become yellow increases markedly with decreasing La/Sn ratio from 8/2 to 6/4. On the other hand, the variation of La/Sn ratio from 6/4 to 0/10 does not influence this time significantly.

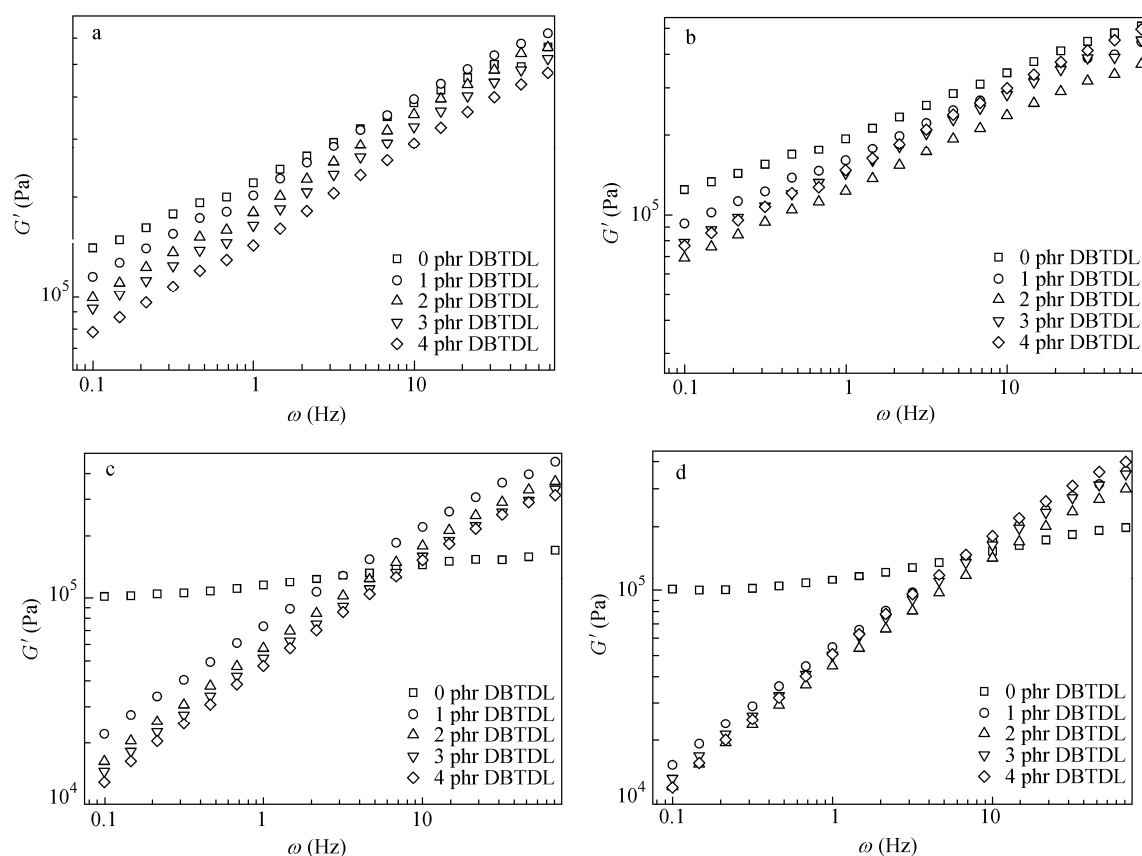


Fig. 6 Influence of DBTDL content on dynamic storage modulus (G') as a function of frequency (ω) for PVC containing different kinds of stabilizers at 180°C: (a) without LaSt_3 and Ca/Zn stabilizers, (b) 2 phr LaSt_3 , (c) 2 phr Ca/Zn stabilizers, and (d) 1 phr LaSt_3 plus 1 phr Ca/Zn stabilizers

Ratio of La/Sn t (min)	0	10	20	30	40	50	60	70	80
10/0									
8/2									
6/4									
4/6									
2/8									
0/10									

Fig. 7 Influence of La/Sn ratio on coloration as a function of time for PVC containing 3 phr La/Sn stabilizers at 180°C

DISCUSSION

FTIR spectra show that A_{3025}/A_{1099} decreases while A_{1730}/A_{1099} increases with increasing DBTDL content, indicating that the content of $\text{C}=\text{C}$ structure in thermal processed PVC reduces gradually^[16, 17], and the

stabilization effect of DBTDL is realized through the substitution to the main chain of PVC^[10–12, 40]. Addition of LaSt₃ to the DBTDL stabilized PVC causes large increases in A_{3025}/A_{1099} and A_{1730}/A_{1099} , indicating that LaSt₃ could partially conceal the stabilization effect of DBTDL even though it can also perform the stabilization effect through the substitution to the main chain of PVC^[41].

$T_{5\%}$ and $T_{\max}$ of PVC at the La/Sn ratio from 8/2 to 0/10 are close to the respective values of the DBTDL stabilized PVC (Fig. 3). The variation of La/Sn ratio from 8/2 to 0/10 does not influence rheological behavior (Fig. 5) and initial coloration (Fig. 7) markedly. The results suggest that the stabilization effect of DBTDL can be achieved by the La/Sn stabilizers with a ratio of 8/2. On the other hand, $T_{5\%}$ and $T_{\max}$ of the LaSt₃ stabilized PVC are far lower than those of the DBTDL stabilized PVC, revealing that DBTDL could not be replaced by LaSt₃ completely. In comparison with using DBTDL in the industry, the partial replacement of DBTDL using LaSt₃ will reduce the cost and toxicity, which is of great importance for PVC industry.

The fact that addition of LaSt₃ or Ca/Zn stabilizers reduces thermal decomposition temperatures (Fig. 4) in comparison with the DBTDL stabilized PVC can be explained by ionization potential of metals. The higher value ionization potential is, the stronger ability the substitution of metal carboxylate to the main chain of PVC possesses^[42]. The values of ionization potential are 9.394, 8.993, 7.344, 6.113, 5.577 and 5.212 eV for Zn, Cd, Sn, Ca, La and Ba, respectively^[43]. The FTIR spectra indicate that LaSt₃ and DBTDL play the role in stabilizing PVC mainly through substitution. Similarly, Ca/Zn stabilizers exhibit stabilization effect through the substitution of ZnSt₂ to the main chain of PVC followed by absorbance of the substitution product ZnCl₂ by CaSt₂^[24, 42]. Due to a higher ionization potential of Zn compared with Sn, ZnSt₂ shows substitution ability stronger than that of DBTDL^[42]. When Ca/Zn stabilizers and DBTDL coexist in the compounds, Ca/Zn stabilizers will be prior to substitute to the main chain of PVC and conceal the stabilization effect of DBTDL, as reported by Garrigues *et al.*^[32] and Guo *et al.*^[33]. Moreover, the stabilization efficiency of Ca/Zn stabilizers appears much weaker compared with that of DBTDL^[44], resulting in large reductions in thermal properties (Fig. 4) in the compounds containing Ca/Zn stabilizers. On the other hand, the substitution ability of LaSt₃ is weaker than that of DBTDL because of the higher ionization potential of Sn. Hence, incorporation of LaSt₃ does not influence the stabilization efficiency of DBTDL markedly. Similar phenomena have been observed and all of them can be explained by the ionization potential of metals^[23–27, 31, 33, 36]. Sn has an ionization potential higher than that of Ca, which can explain the speculation of Guo *et al.*^[33] that organotin stabilizer is more active than CaSt₂ in stabilizing PVC. Similarly, ionization potentials of Zn and Cd are higher than those of Ba and Ca so that the reaction rates of Cd and Zn carboxylates with unstable chloride are largely quicker than those of Ba and Ca carboxylates^[45]. Moreover, Zn has a higher ionization potential than that of La and Ca. ZnSt₂ will be prior to react with unstable chloride, and the product ZnCl₂ can be absorbed by CaSt₂ or LaSt₃, which can account properly for the synergistic effect of Ca/Zn stabilizers^[23–27] and La/Zn stabilizers^[31].

In comparison with the aforementioned phenomena about organotin stabilizers in combination with co-stabilizers reported in the references, influences of LaSt₃ and Ca/Zn stabilizers on the stabilization efficiency of DBTDL are studied in detail and explained in the framework of ionization potential. It is found that incorporation of LaSt₃ does not influence the stabilization efficiency of DBTDL while addition of Ca/Zn stabilizers leads to a large reduction in thermal property, which replies that DBTDL can not be replaced by Ca/Zn stabilizers but it can be partly replaced by LaSt₃.

CONCLUSIONS

The partial replacement of DBTDL using LaSt₃ could maintain the stabilization efficiency of PVC. The stabilization effect can be achieved by the La/Sn stabilizers with a ratio of 8/2 on the basis of thermal properties. However, thermal decomposition temperatures of the LaSt₃ stabilized PVC are far lower than those of the DBTDL stabilized PVC, revealing that DBTDL can not be replaced by LaSt₃ completely. Addition of DBTDL can improve thermal property and reduce G' for PVC containing LaSt₃ or Ca/Zn stabilizers due to the strong stabilization effect of DBTDL. Because of the higher ionization potential of Sn compared with La, the

substitution ability of LaSt₃ is weaker than that of DBTDL so that incorporation of LaSt₃ does not influence the stabilization efficiency of DBTDL markedly. On the other hand, due to the higher ionization potential of Zn compared with Sn, the stabilization effect of DBTDL is concealed by ZnSt₂, which results in the fact that incorporation of Ca/Zn stabilizers into DBTDL stabilized PVC causes a large reduction in thermal properties.

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