

## تأثیر پنتا اریتریتول و ارگانوتین با استئارات کلسیم و استئارات روی، روی پایداری حرارتی PVC

امروزه پایدار کننده حرارتی استئارات کلسیم /روی برای پایداری حرارتی PVC به طور وسیعی استفاده می شود. استئارات کلسیم یک پایدار کننده حرارتی طولانی مدت برای PVC است که به تنهایی باعث تغییر رنگ زود هنگام و ناگهانی در PVC می شود. این در حالی است که استئارات روی باعث تغییر رنگ ناگهانی نمی شود و رنگ اولیه خوبی در PVC ایجاد می کند، اما در مراحل بعدی باعث تغییر رنگ می شود. در نتیجه استئارات کلسیم و استئارات روی مکمل یکدیگر بوده و اکثراً همزمان استفاده می شوند.

اما این دو نیاز به یک پایدار کننده ثانویه هم دارند که باعث بهبود رنگ اولیه در PVC می شود. مانند پلی اول ها، هیدرو تالسیت، زئولیت و روغن های اپوکسی شده که همگی به عنوان پایدار کننده ثانویه همزمان با سیستم کلسیم/روی استفاده می شوند. در این مقاله پنتا اریتریتول و ارگانوتین به عنوان کمک پایدار کننده به سیستم کلسیم/روی در PVC افزوده شدند.

نتایج نشان داد که ترکیب پنتا اریتریتول و ارگانوتین با کلسیم/روی خواص حرارتی و رنگ اولیه PVC را بهبود می دهد. افزایش تأثیر پایدار کنندگی کلسیم/روی به خاطر تأثیر کلسیم روی و پت اریتریتول و برهمکنش بین ارگانوتین و باندهای دوگانه تشکیل شده در حین تخریب PVC است. ارگانوتین و پنتا به تنهایی به پایداری کمک نمی کنند و ارگانوتین و کلسیم/روی نیز به تنهایی موثر نیستند.

# Effect of pentaerythritol and organic tin with calcium/zinc stearates on the stabilization of poly(vinyl chloride)

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## Abstract

The stabilization effect of calcium and zinc stearates ( $\text{CaSt}_2/\text{ZnSt}_2$ ) combined with pentaerythritol (PeE) and organic tin on poly(vinyl chloride) was investigated. The results show that the addition of calcium/zinc stearates combined with PeE and organic tin can improve thermal and colour stability of poly(vinyl chloride) in both static and dynamic tests. Mechanisms for improving stability of PVC are also discussed. The increase of stabilizing effectiveness of calcium/zinc stearates is ascribed to the synergistic effect between  $\text{CaSt}_2/\text{ZnSt}_2$  and PeE and the interaction between organic tin and double bonds formed during the degradation of PVC. There is no synergistic action between organic tin and PeE or organic tin and calcium/zinc stearates.

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*Keywords:* Calcium and zinc stearates; Organic tin; Pentaerythritol; Thermal stabilizer; Poly(vinyl chloride)

## 1. Introduction

Recently, calcium and zinc stearates ( $\text{CaSt}_2/\text{ZnSt}_2$ ) are widely used to prevent poly(vinyl chloride) (PVC) from undergoing dehydrochlorination at its processing temperature.  $\text{CaSt}_2$ , an alkaline earth metal soap, prolongs the long-term heat stability of PVC but does not impart good initial colour; while  $\text{ZnSt}_2$ , a covalent metal soap, prolongs initial colour but leads to subsequent discolouration. When  $\text{CaSt}_2$  and  $\text{ZnSt}_2$  are used together for stabilizing PVC, they show a good synergistic effect [1,2]. A complex which inhibits degradation of PVC is formed when  $\text{CaSt}_2$  and  $\text{ZnSt}_2$  are pre-heated at their melting temperature [3–6].

Although  $\text{CaSt}_2$  and  $\text{ZnSt}_2$  exhibit synergistic effect, the success of the  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizers is undoubtedly attributed to the incorporation of organic synergists or secondary stabilizers. Polyols [7–11] and  $\beta$ -diketones [12–14], which have the effect of improving the initial colour of the PVC and the efficiency of  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizers for PVC, are normally added as synergists to  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizing systems.

Epoxidised sunflower oil (ESO) [15], hydrotalcites [16], zeolites [17] and inorganic phosphates [18] were also reported to show co-stabilization with  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizers.

Pentaerythritol (PeE) is an important secondary stabilizer for  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizers, and many researchers [19,20] have reported excellent studies. Briggs and Wood [19] proposed that PeE formed complexes with zinc chloride to delay the “zinc burning”, but the complexes were undetermined. Abbas and Sörvik [20] thought that PeE might react directly with HCl to remove free HCl from the system. Although PeE had some synergistic effect with the metal soaps, the action mechanism was not very well understood.

Studies on interaction effect between organic tin and  $\text{CaSt}_2/\text{ZnSt}_2$  system were hardly reported. Garrigues et al. [21] considered that some reactions between zinc chloride and organic tin happened during the PVC processing. The product, organic tin chloride, which was also a Lewis acid, was less powerful as a dehydrochlorination catalyst compared with zinc chloride.

In this work, pentaerythritol (PeE) and organic tin were used to improve the efficiency of  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizers for PVC. The influences of PeE or organic tin upon the co-stabilization effect for PVC and the effect mechanism were further

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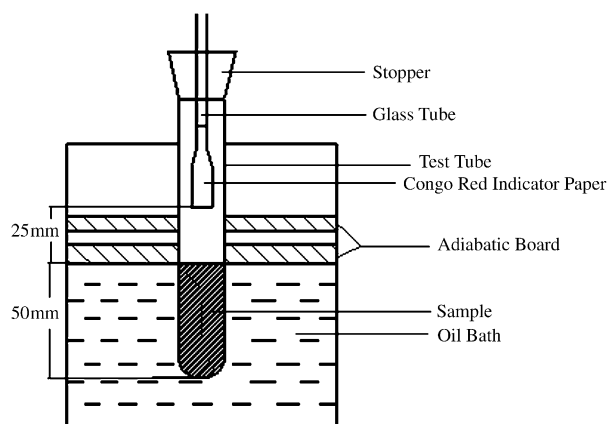


Fig. 1. Schematic representation of the device for Congo red test.

investigated. The effectiveness of PeE was described by Congo red discoloration time, Fourier transform infrared (FTIR) and Yellowness index testing; while the effectiveness of organic tin was analyzed by Haake plasticorder, UV–visible and energy dispersive X-ray analysis.

## 2. Experimental

### 2.1. Materials

The PVC used in this work was PVC-SG5 supplied by Yibing TianYun Co. Ltd., Sichuan, China.  $ZnSt_2$  (from Yuanhang Chemical Reagent Plant, Shanghai, China) and  $CaSt_2$  (from Tianjin Chemical Reagent Plant, Tianjin, China) were used as stabilizers; PeE (from Kelong Chemical Reagent Plant, Chengdu, Sichuan, China) and mercaptan tin (from Beijing Elf Ato Chemical Co. Ltd., China), an organic tin, were used as co-stabilizers.

### 2.2. Sample preparation

Hundred parts of PVC, synergistic metal soap mixture which includes  $CaSt_2/ZnSt_2$  (2/3) complex (powder, 2.5 phr), organic tin (liquid, 0.1–0.3 phr) and PeE (powder, 0.5 phr)

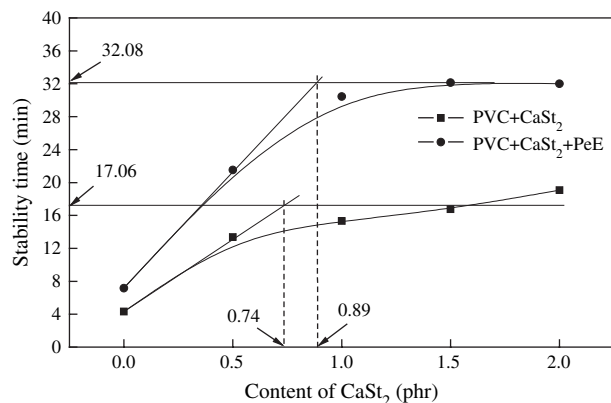


Fig. 2. Effect of PeE (0.5 phr) on the stability time of PVC compound (PVC +  $CaSt_2$ ).

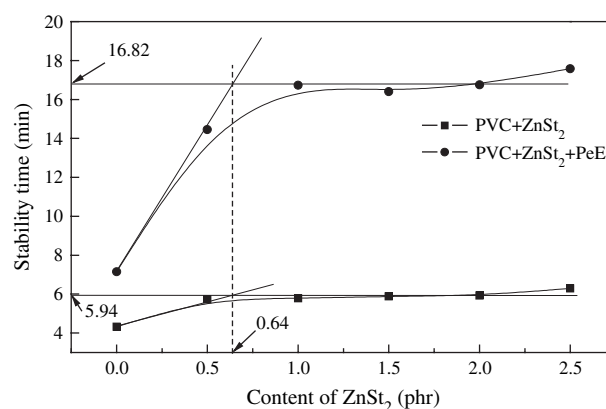


Fig. 3. Effect of PeE (0.5 phr) on the stability time of PVC compound (PVC +  $ZnSt_2$ ).

were dry blended. The ca. 10 g mixture was used for Congo red test. Then, the rest mixture was milled by an open twin-roller at 170 °C for 5 min. The compressed PVC sheet, with ca. 1.0 mm thickness, was prepared and cut into circular sheets (diameter: 14 mm) and the rectangular sheets (50 × 50 mm). The circular sheets were used for discoloration time test, and the rectangular sheets for yellowing index test.

### 2.3. Measurements

According to the standard of ASTM D4202, the schematic diagram of the Congo red testing device is described in Fig. 1. Glycerol was used as oil bath. The test temperature was 180 °C. This method was used for static thermal stability analysis.

For dynamic thermal stability analysis in the open processing environment, PVC/thermal stabilizers mixture was milled in an open twin-roller at 170 °C. The mixture was milled till its colour turned black. The dynamic thermal stabilizing time is defined as the time when its colour starts to turn black, and is termed the blackening time of milling.

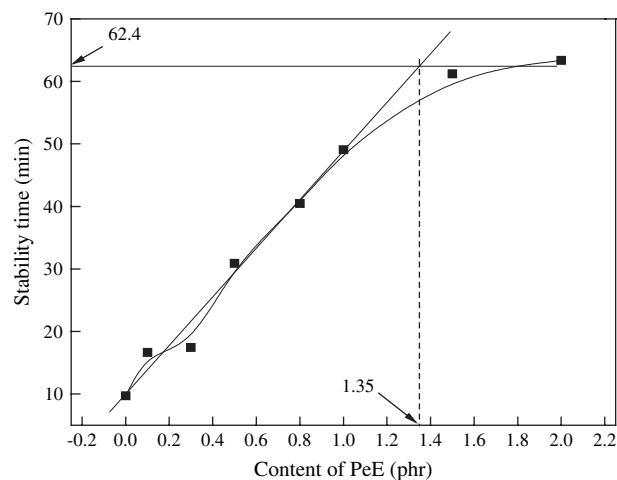


Fig. 4. Effect of PeE on the stability time of PVC compound (PVC +  $CaSt_2/ZnSt_2$  2.5 phr).

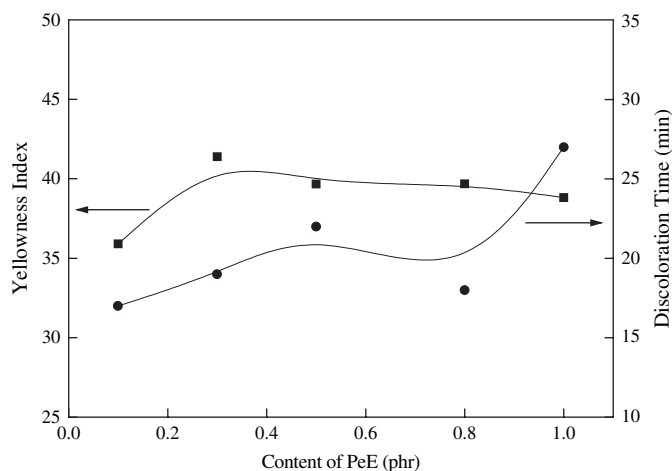


Fig. 5. Effect of PeE on discoloration time and Yellowness index of PVC compound (PVC + CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr).

For dynamic thermal stability analysis in the closed processing environment, PVC/thermal stabilizer mixture was tested in the mixing chamber of a Haake Rheometer RC90 at 170 °C and a rotor speed of 30 rpm for 20 min. The dynamic thermal stabilizing time is defined as the time when the torque on the rotor starts to change abruptly.

The sample for discoloration time test was prepared on an open twin-roller at 170 °C for 5 min. According to the standard ISO 305:1990, the PVC sheet, about 1.0 mm thickness, was cut into the circular sheets (diameter: 14 mm) for testing. Glycerol was used as oil bath, and the test temperature was 180 °C.

According to the standard GB2409-80, the Yellowness index was measured by the Tristimulus Colorimeter SC-80A in order to study the colour stability of PVC samples. The thermal stabilizers and PVC were mixed, and then pressed into thin sheets of 1.0 mm thickness using an open twin-roller at 170 °C for 5 min.

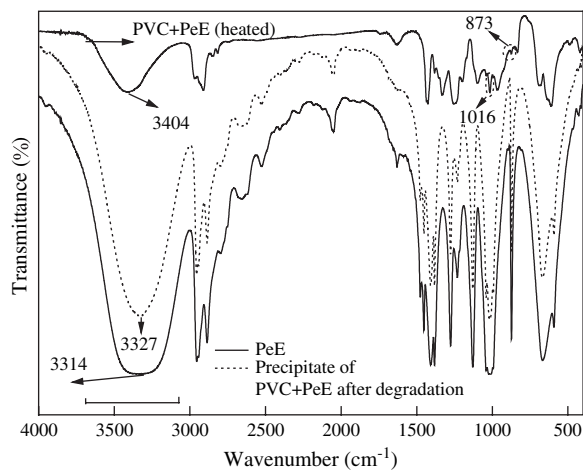


Fig. 6. FTIR spectra of PVC and PeE samples. Formulation of PVC/PeE blend: PVC 100 phr, PeE 0.5 phr.

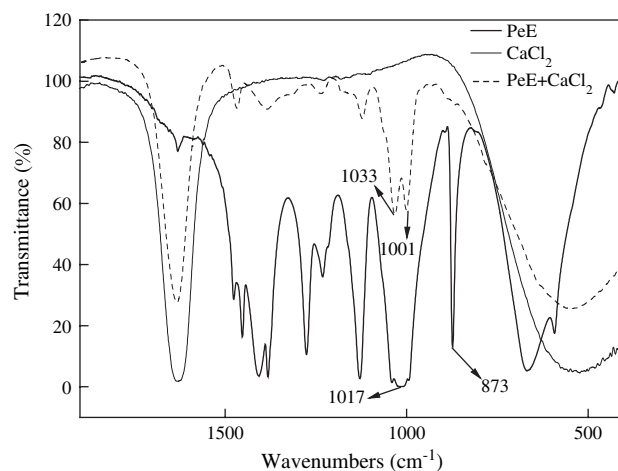


Fig. 7. FTIR spectra of CaCl<sub>2</sub> and PeE samples. Formulation of CaCl<sub>2</sub>/PeE blend: CaCl<sub>2</sub> 1 phr, PeE 0.5 phr.

The interaction between PeE and PVC was analyzed by Fourier transform infrared (Nicolet-560 FTIR). Approximately 1.0 mg sample added with ca. 200 mg dried KBr was ground in an agate bowl, then pressed into a transparent slice by a ca. 400 kg/cm<sup>2</sup> pressure for about 2 min. The slice was dried for about 2 min before testing. Forty scans were acquired at a resolution of 1 cm<sup>-1</sup>.

A UV spectrophotometer (UV-2100, Shimadzu Co. Ltd., Japan) was used to obtain the UV spectra for PVC samples, which were dissolved in tetrahydrofuran (THF), in order to investigate the content of double bonds.

Energy dispersive X-ray analysis (EDAX9100160, Hitachi Co. Ltd., Japan) was used to obtain the contents of sulfur and tin. The PVC with organic tin samples, which were dissolved in tetrahydrofuran (THF), was heated for 3 h at 200 °C or unheated, and then precipitated by absolute alcohol.

### 3. Results and discussions

#### 3.1. Effect of PeE on the stabilizing system

In order to confirm which component of the CaSt<sub>2</sub>/ZnSt<sub>2</sub> stabilizing system had more synergistic effect with PeE, PeE was added into CaSt<sub>2</sub>, ZnSt<sub>2</sub> and CaSt<sub>2</sub>/ZnSt<sub>2</sub> (2/3) as a co-stabilizer for PVC stability testing. The stability time of PVC/different stabilizers was obtained by Congo red test. The results indicated that PeE had a synergistic effect with

Table 1  
SEC value of various stabilizer systems

Sample	SEC (phr)
PVC-SG5+	
CaSt <sub>2</sub>	0.74 (CaSt <sub>2</sub> ), see Fig. 2.
ZnSt <sub>2</sub>	0.64 (ZnSt <sub>2</sub> ), see Fig. 3.
CaSt <sub>2</sub> + PeE	0.89 (CaSt <sub>2</sub> ), see Fig. 2.
ZnSt <sub>2</sub> + PeE	0.64 (ZnSt <sub>2</sub> ), see Fig. 3.
CaSt <sub>2</sub> /ZnSt <sub>2</sub>	2.40 (CaSt <sub>2</sub> /ZnSt <sub>2</sub> ), see Fig. 11.
CaSt <sub>2</sub> /ZnSt <sub>2</sub> + PeE	1.35 (PeE), see Fig. 4.

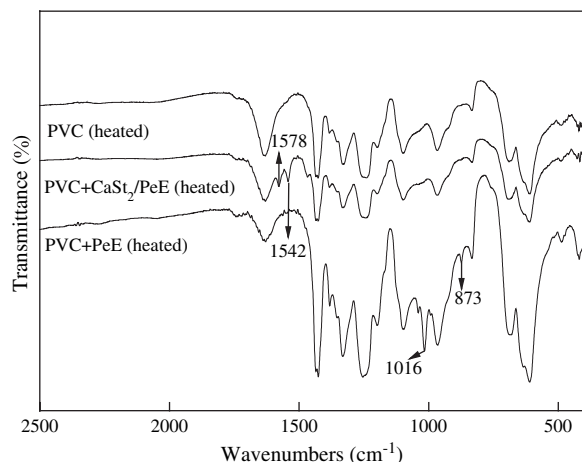


Fig. 8. FTIR spectra of PVC,  $\text{CaSt}_2$  and PeE samples. Formulation of PVC/ $\text{CaSt}_2$ /PeE blend: PVC 100 phr,  $\text{CaSt}_2$  1 phr, PeE 0.5 phr. Formulation of PVC/PeE blend: PVC 100 phr, PeE 0.5 phr.

$\text{CaSt}_2$ ,  $\text{ZnSt}_2$  and  $\text{CaSt}_2/\text{ZnSt}_2$ , respectively, as shown in Figs. 2–4. In the absence of  $\text{CaSt}_2$ ,  $\text{ZnSt}_2$  or  $\text{CaSt}_2/\text{ZnSt}_2$ , PeE had little effect on the increase of the stability time. A colour change of the indicator paper took place in a short heating time. Stability time increased when PeE was added to the  $\text{CaSt}_2$ ,  $\text{ZnSt}_2$  or  $\text{CaSt}_2/\text{ZnSt}_2$  system. The  $\text{CaSt}_2/\text{ZnSt}_2$  in the weight ratio of 2/3 when used in combination with PeE was found to be the most effective in improving the stability time of PVC.

For the  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizing system, when the content of PeE increased to above 1.35 phr, the stability time obtained by Congo red testing (Fig. 4) was too long to indicate the result exactly. Discolouration time and Yellowness index analyses were used to confirm the effect. The results showed that the increased amount of PeE obviously prolonged the discolouration time but indistinctly decreased the Yellowness index (Fig. 5), indicating that PeE improves the processing stability of PVC with  $\text{CaSt}_2/\text{ZnSt}_2$  (2/3) stabilizing system, but has no obvious effect on colour stability.

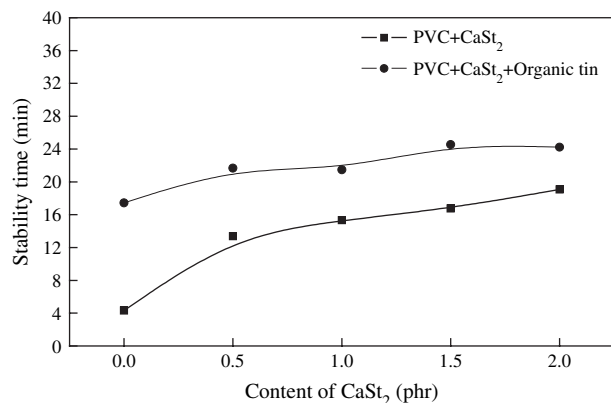


Fig. 9. Effect of organic tin (0.2 phr) on the stability time of PVC compound (PVC +  $\text{CaSt}_2$ ).

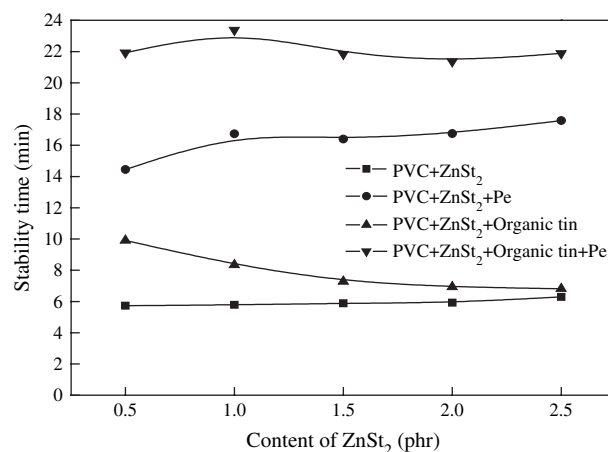
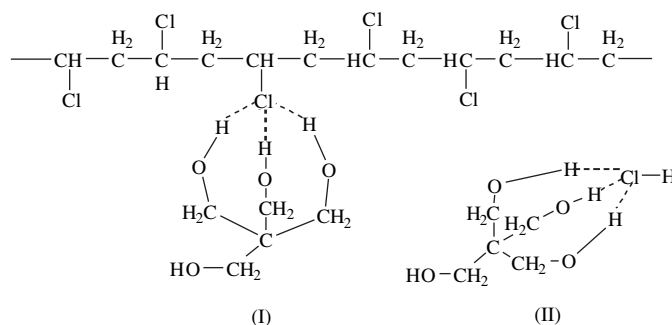


Fig. 10. Effect of organic tin (0.2 phr) and PeE (0.5 phr) on the stability time of PVC compound (PVC +  $\text{ZnSt}_2$ ).

It is clear from these results that good stabilization effects of PeE could be observed on the PVC with  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizing system, which was ascribed to the action that the PeE served as an acceptor or chelating agent for the metal chloride produced from  $\text{CaSt}_2$  and  $\text{ZnSt}_2$  to retard the abrupt degradation of PVC. The synergistic effect of PeE to the  $\text{CaSt}_2/\text{ZnSt}_2$  stabilizing system is discussed below.

Comparing pure PVC, the stability time of PVC with PeE solely had a little improvement from 4.19 min to 7.15 min (Figs. 2 and 3), but the reason was unclear. In our opinion, there are two possible reasons. One is that the interaction between the alcoholic hydrogen of the PeE and the labile chlorine atom of PVC chains makes the dehydrochlorination difficult to a certain extent. The chlorine atom in the PVC chains has three pairs of non-bonded electrons, which can accept hydrogen atoms with unfilled orbitals, as shown in the structure (I) (a dashed line represents that there may be some interaction between two atoms, here and in the following structures). Another is that PeE can trap the free HCl by the same effect between hydrogen atoms and chlorine atom like the structure (II). It is well known that this intermolecular interaction is very weak and can exist only in short time at PVC processing temperature (170–180 °C), which was exhibited in that the improvement of stability time was from 4.19 min to 7.15 min.



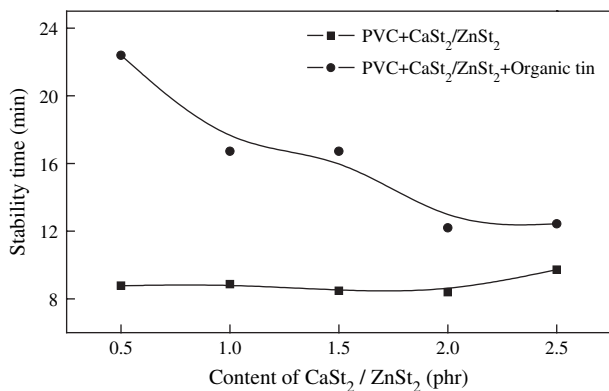


Fig. 11. Effect of organic tin (0.2 phr) on the stability time of PVC compound (PVC + CaSt<sub>2</sub>/ZnSt<sub>2</sub>).

In order to prove the interaction between PVC and PeE, FTIR analysis was used. Pure PeE and PVC/PeE (100/0.5) compound heated in the 180 °C glycerol bath for 5 min was prepared for the test. The spectra showed that a broad peak (from about 3700 cm<sup>-1</sup> to 3080 cm<sup>-1</sup>) of the –OH stretching vibration band in the pure PeE became sharp in the PVC/PeE compound. Moreover, the wavenumber of the –OH band shifted from 3314 cm<sup>-1</sup> to 3404 cm<sup>-1</sup> (as shown in Fig. 6). The results indicated that the interaction between PVC and PeE could destroy the intermolecular or intramolecular H-bonding of PeE molecules to make a change of the –OH peak shape and a shift of the –OH band. Due to this interaction, the stability for the PVC added with PeE was better than pure PVC. This gave a proof for our opinion.

In another test, the solubility of PVC/PeE compound (0.5 g) after degradation in tetrahydrofuran (THF) (30 ml) at 25 °C was examined. The degradation was defined when the colour of the indicator paper turned blue. After 2 days, there were still some precipitates at the bottom of the test tube. Because PeE couldn't dissolve in THF and the appearance of the precipitates looked much like PeE, it is inferred that the residual matter was PeE. The FTIR was used to clarify it. The FTIR results

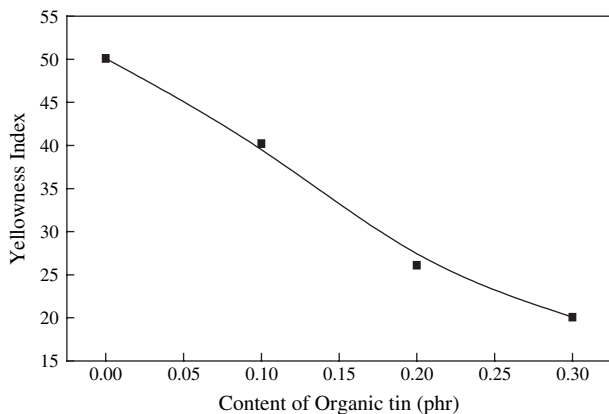


Fig. 12. Curve of Yellowness index of PVC sheets (PVC + CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr) vs. content of organic tin.

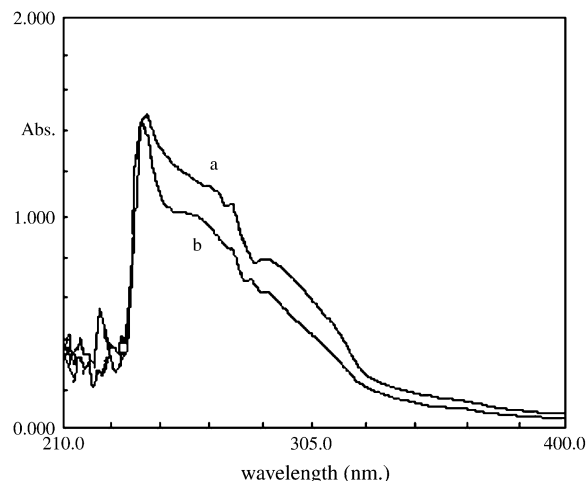


Fig. 13. UV spectra of PVC samples. Formulation a: PVC 100 phr, CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr; Formulation b: PVC 100 phr, CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr, organic tin 0.2 phr.

showed that there were no PVC molecules in the precipitates and the spectra of the precipitates were very similar to that of the PeE (Fig. 6) indicating that crosslinking between PVC chains did not happen in the degradation and the interaction between PeE and PVC was not covalent bonding but only intermolecular H-bonding. These gave an additional proof for our opinion.

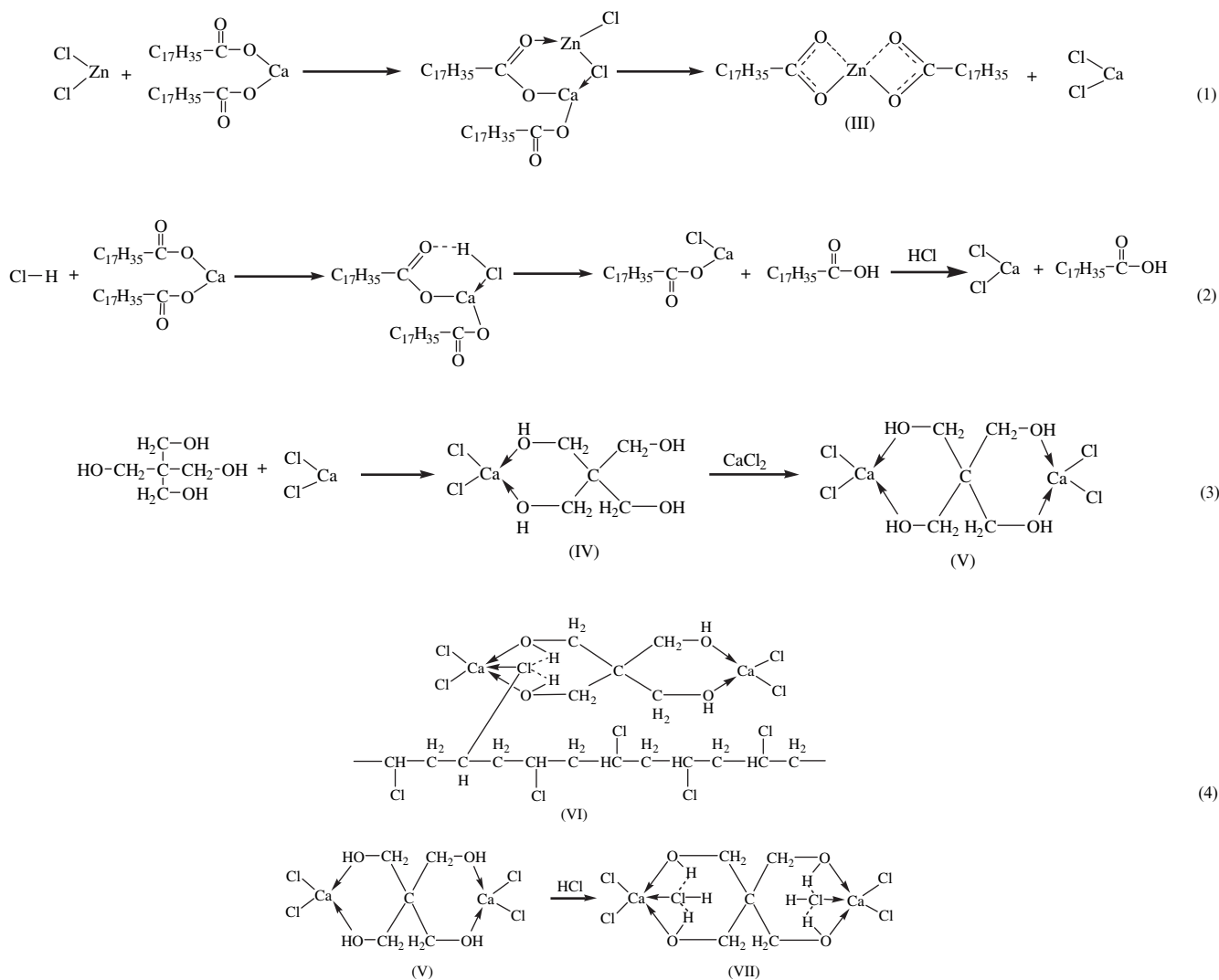
The effect mechanism between PeE and CaSt<sub>2</sub> was also discussed. CaSt<sub>2</sub> as an alkaline earth carboxylate does not substitute the labile chlorine atoms of PVC chains but serves to regenerate the active stabilizer (ZnSt<sub>2</sub>) and removes the potentially destructive effect of the ZnCl<sub>2</sub> (reaction (1)). It can also react with the HCl which itself is thought to catalyse dehydrochlorination (reaction (2)). When CaSt<sub>2</sub> together with PeE was added into PVC, they exhibited the synergistic effect to improve PVC stability as shown in Fig. 2. It was inferred that there were some interaction among PeE, CaSt<sub>2</sub> and CaCl<sub>2</sub> produced by reactions (1) and (2). In our point of view, the interaction between PeE and CaCl<sub>2</sub> was a main reason for the synergistic effect, which was discussed below.

It is because the calcium atom of CaCl<sub>2</sub> has many unfilled orbitals and the oxygen atom of PeE has several pairs of non-bonded electrons that the interaction between the two atoms can easily happen. Also, since the six-membered ring structure is comparatively stable, it is possible that the interaction may form a complex like structure (IV) or (V). Moreover, it can be inferred from the experimental results (Fig. 2) that there may exist coordinate bonding between Ca atom and Cl atom of PVC, which is much stronger than hydrogen bonding and can exist for a longer time at the PVC processing temperature; then, the structures (VI) and (VII) are more stable than structures (I) and (II), respectively. The stability time of PVC/CaSt<sub>2</sub>/PeE system was much longer than the total time of PVC/PeE system and PVC/CaSt<sub>2</sub> system.

In order to prove the possibility of structure (IV) or (V), Pure PeE, pure CaCl<sub>2</sub> and the PeE/CaCl<sub>2</sub> mixture (0.5/1) was analyzed by FTIR after heating for 5 min at 180 °C. It

was shown that the C–O band of PeE ( $1017\text{ cm}^{-1}$ ) split into two peaks ( $1033\text{ cm}^{-1}$ ,  $1001\text{ cm}^{-1}$ ) and the characteristic peak of PeE ( $873\text{ cm}^{-1}$ ) disappeared in the PeE/CaCl<sub>2</sub> mixture (Fig. 7), indicating that the two compounds may form a complex like structure (IV) or (V).

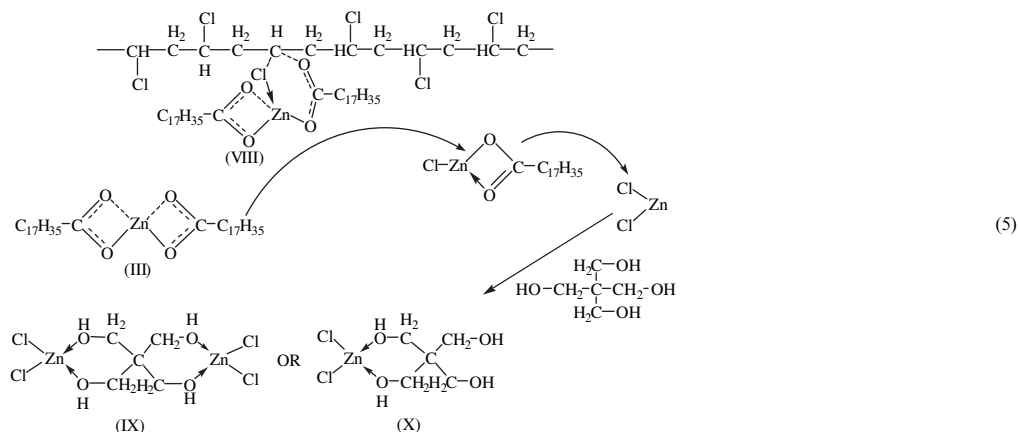
Based on the structure of zinc stearate, Tsutomu Ishioka et al. [22] pointed out that the coordination number of the carboxylate groups around the zinc atom was evaluated as 4 and the form of the carboxylate groups was determined as bridging bidentate type. Combining this investigation with our previous



Comparing the spectra of PVC/PeE blend, the characteristic peak ( $873\text{ cm}^{-1}$ ) and C–O stretching vibration band ( $1016\text{ cm}^{-1}$ ) of PeE disappeared in PVC/CaSt<sub>2</sub>/PeE system as shown in Fig. 8. These indicate that some reactions happened among PVC, CaSt<sub>2</sub> and PeE like reactions (2)–(4) and structure (VI).

Like PVC/PeE compound, the PVC/CaSt<sub>2</sub>/PeE compound after degradation was added to THF to dissolve. After 2 days, there were no precipitates in the test tube; the compound after degradation was completely soluble. This result indicates that crosslinking did not happen in the degradation processing and some reactions might happen among PVC, CaSt<sub>2</sub> and PeE, like reactions (2)–(4).

study [6], the structure of zinc stearate is described as structure (III) in reactions (1) and (5). The stabilizing effect of ZnSt<sub>2</sub> to PVC may be ascribed to formation of a six-membered ring complex (structure (VIII)) and then replacement of the labile chlorine atom with more stable carboxylate groups. The zinc chloride having Lewis acid character produced by this reaction can act as a catalyst for PVC degradation. Therefore, the stability time of PVC was very short and the “zinc burning” happened. The stability time increased abruptly with the existence of PeE (Fig. 3). According to our previous study [6], the main factor was inferred to be that PeE showed an accepting or chelating mechanism with zinc chloride to form an inactive complex (structure (IX) or (X)).



### 3.2. Starting effect content of stabilizers analysis

To prevent the degradation of PVC, stabilizers or other reagents with stabilizing effect are added into the PVC formulation. The appropriate amount of the added composition is very important. In order to confirm the most appropriate contents of the additives, the starting effect content (SEC) is defined. The stability time of PVC compound can be divided into two sections: an initial low effect followed by an obviously improvement on the stability time. The SEC value is obtained graphically from the intersection of the two extrapolations (Figs. 2 and 3). For PVC/CaSt<sub>2</sub>, the SEC value of CaSt<sub>2</sub> is 0.74 phr. In other words, the appropriate added amount of CaSt<sub>2</sub> to the PVC/CaSt<sub>2</sub> compound is above 0.74 phr. Table 1 shows the SEC value of PVC/different stabilizers. From the data in Table 1, it is more convenient to choose the appropriate added content.

### 3.3. Effect of organic tin on the stabilizing system

Like PeE, organic tin was added into CaSt<sub>2</sub>, ZnSt<sub>2</sub> and CaSt<sub>2</sub>/ZnSt<sub>2</sub> as a stabilizer system for stability testing. Figs. 9–11 show the effect of organic tin with CaSt<sub>2</sub>, ZnSt<sub>2</sub> and CaSt<sub>2</sub>/ZnSt<sub>2</sub> stabilizing systems, respectively. There is no

synergistic effect observed in the above stabilizing systems with organic tin. The stabilizing effect of organic tin and the above stabilizing systems acts simultaneously.

The stability time of PVC/CaSt<sub>2</sub> compound with organic tin was longer than that without organic tin, but the value is close to that of PVC/organic tin compound (Fig. 9). CaSt<sub>2</sub> has not exhibited its effect on PVC. That is, organic tin may be more active than CaSt<sub>2</sub> in stabilizing PVC. Its correspondingly active effect conceals the effect of CaSt<sub>2</sub>.

Compared with CaSt<sub>2</sub>, the stability time of PVC/ZnSt<sub>2</sub> compound with organic tin was also investigated. The compound added with organic tin improves slightly the thermal stability of PVC. The stabilizing effect of organic tin is much slower than the dehydrochlorination accelerated by the zinc chloride, which is formed by ZnSt<sub>2</sub> during the stabilizing process. When PeE as a chelating agent of zinc chloride was added into the PVC/ZnSt<sub>2</sub>/organic tin compound to weaken the catalysis of zinc chloride, the stability time increased obviously (Fig. 10). It can be also concluded that ZnSt<sub>2</sub> may be more active than organic tin in stabilizing PVC. The similar situation can be observed in the effect between organic tin and CaSt<sub>2</sub>/ZnSt<sub>2</sub> (Fig. 11). Organic tin can improve the colour stability of the PVC and CaSt<sub>2</sub>/ZnSt<sub>2</sub> compound, although it is

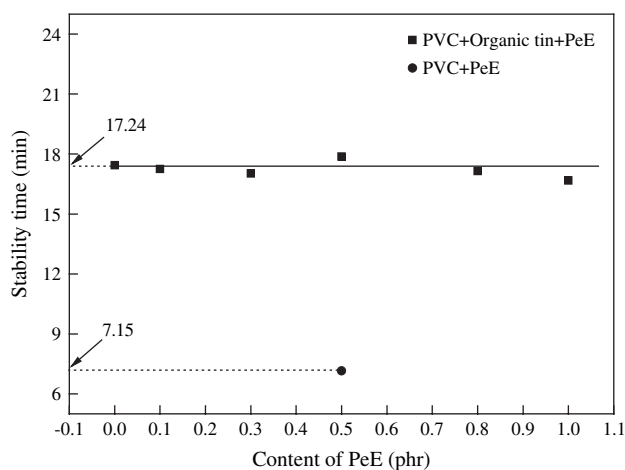


Fig. 14. Effect of PeE on the stability time of PVC compound (PVC + organic tin 0.2 phr).

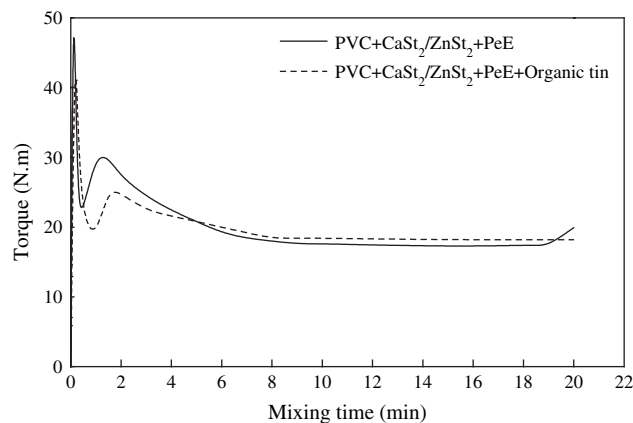


Fig. 15. Dynamic thermal stability test for PVC compound. Formulation a: PVC 100 phr, CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr, PeE 0.5 phr (solid line). Formulation b: PVC 100 phr, CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr, PeE 0.5 phr and organic tin 0.2 phr (dashed line).



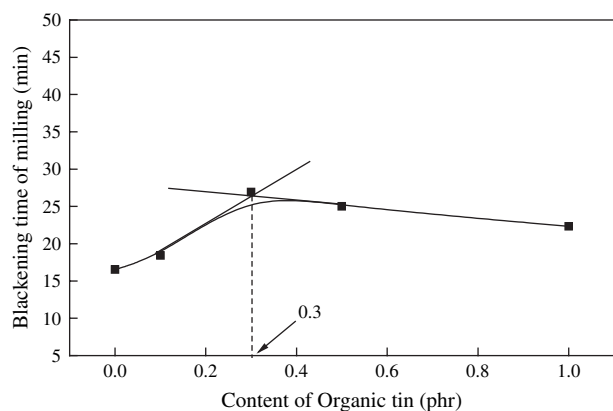


Fig. 16. Curve of blackening time of milling vs. content of organic tin. The compounds (PVC 100 phr, PeE 0.5 phr and CaSt<sub>2</sub>/ZnSt<sub>2</sub> 2.5 phr) with various content of organic tin were milled in the twin-roller at 170 °C.

difficult to improve the thermal stability of the compound, as shown in Fig. 12.

UV–visible and energy dispersive X-ray analysis was used to confirm the effect mechanism of organic tin. It is clear from Fig. 13 that UV curve b (with organic tin) moves toward the shorter wavelength direction, indicating that the amount of the conjugated bonds of PVC decreases obviously due to the incorporation of organic tin. It means that the organic tin can react with double bonds formed during the degradation of PVC samples. Energy dispersive X-ray analysis result shows that there exists 6.66% tin and 9.33% sulfur element in heated PVC with organic tin sample, while 9.57% tin and 5.87% sulfur element in unheated sample, indicating that there is interaction between PVC and organic tin due to the increased content of sulfur element. In our point of view, C–S bonds are formed during the PVC processing due to the incorporation of organic tin. Organic tin can replace the labile chlorine atoms of the PVC chains with more stable mercaptide groups (reaction (6)), and another reaction with HCl to produce mercaptan (reaction (7)), which addition reacts with double bonds formed during the degradation of PVC samples (reaction (8)).

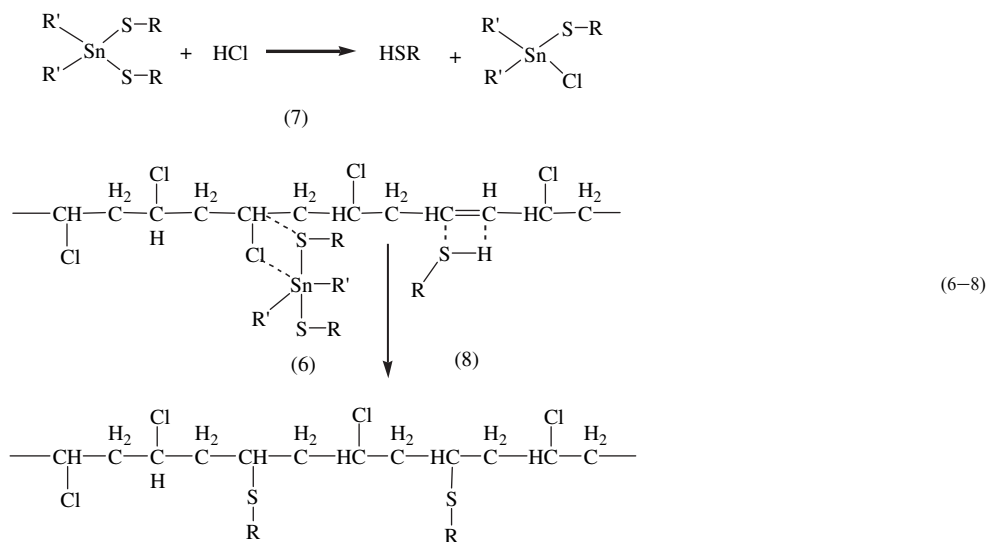
#### 3.4. Effect of organic tin together with PeE as the stabilizing system

Before studying the effect of organic tin together with PeE for the stabilizing system, the interaction between organic tin and PeE should be investigated. Fig. 14 shows the effect of PeE on the stability time of PVC/organic tin compound. Like CaSt<sub>2</sub>, the effect of PeE was not revealed due to the presence of organic tin. Both the stabilizing effects to PVC may begin at the same time, but end at different time. Therefore, the effect of organic tin was just observed in PVC/PeE/organic tin compound.

Furthermore, the stabilizing effect of CaSt<sub>2</sub>/ZnSt<sub>2</sub> stabilizing system together with PeE and organic tin was observed by the HAAKE Rheometer RC90. The addition of organic tin to the CaSt<sub>2</sub>/ZnSt<sub>2</sub> and PeE system increased the time stability from 19 min (CaSt<sub>2</sub>/ZnSt<sub>2</sub> and PeE) to above 20 min (CaSt<sub>2</sub>/ZnSt<sub>2</sub>, PeE and organic tin) as shown in Fig. 15. In order to observe the colour after mixing, the test time was limited within 20 min. The colour of the formulation with organic tin was primrose yellow, but the formulation without organic tin was black due to the occurrence of “zinc burning”. This figure shows that the organic tin added to the formulation can prolong the degradation of PVC and improve colour stability. The SEC of the organic tin to the PVC, CaSt<sub>2</sub>/ZnSt<sub>2</sub> and PeE compound was investigated by the open twin-roller as shown in Fig. 16, and its value is 0.3 phr.

#### 4. Conclusions

Pentaerythritol (PeE) showed excellent properties as a secondary stabilizer for PVC when used in combination with CaSt<sub>2</sub>/ZnSt<sub>2</sub> stabilizing system. PeE exhibited synergistic effect to CaSt<sub>2</sub>, ZnSt<sub>2</sub> and CaSt<sub>2</sub>/ZnSt<sub>2</sub> stabilizers, while it showed a little stabilizing effect when added solely into PVC. That is, PeE acts as an acceptor or chelating agent for metal chloride to form an inert complex.



Organic tin can prolong the degradation of PVC and improve colour stability due to replacement of the labile chlorine atoms with more stable mercaptide groups and react directly with HCl to form mercaptan which can happen addition reaction with double bonds. Different to PeE, organic tin showed no synergistic effect with the above stabilizing systems. Both the stabilizing effects of organic tin and the above stabilizing systems act simultaneously. The features can be summarized that organic tin was more active than CaSt<sub>2</sub> or PeE in stabilizing PVC, while ZnSt<sub>2</sub> was the most active.

The starting effect content (SEC) is defined in order to confirm more appropriate content of the additives. For PVC/PeE/CaSt<sub>2</sub>/ZnSt<sub>2</sub>, the SEC value of organic tin is 0.3 phr.

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