ORIGINAL ARTICLE

Synergism of pentaerythritol-zinc with β-diketone and calcium stearate in poly(vinyl chloride) thermal stability

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Pentaerythritol-zinc (called Penzinc), which is a novel thermal stabilizer for PVC, was synthesized, and its performance was characterized during the thermal processing of PVC. The stabilization effects of this new stabilizer combined with calcium stearate (CaSt₂) and stearoyl benzoyl methane (β -diketone) were investigated using conductivity tests, thermal aging tests, and torque rheometry tests. The results revealed that the addition of Penzinc can improve the color and thermal stability of PVC in both static and dynamic tests. There are no obvious synergistic effects between Penzinc and CaSt₂. However, the synergistic action between Penzinc and β -diketone is excellent. The thermal stability mechanisms of Penzinc and β -diketone are also discussed with the help of quantum chemical calculations.

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Keywords: PVC; pentaerythritol-zinc; β -diketone; synergism; quantum chemical calculations; thermal stability mechanism

INTRODUCTION

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Poly(vinyl chloride) (PVC) is an extensively used thermoplastic material because of its valuable properties, such as superior mechanical and physical properties and its high chemical and abrasion resistance, and it is widely utilized in applications that require durability.^{1,2} PVC undergoes degradation during its processing. The degradation of PVC usually proceeds through a dehydrochlorination process, which results in the formation of long conjugated double bonds or polyene sequences, $-(-CH = CH-)-_n$, which causes a color change.^{3,4} Various methods have been developed to address this problem. Among these methods, the most efficient and practical is the addition of thermal stabilizers to PVC to protect against thermal degradation.⁵ The adequate selection of thermal stabilizers for the polymer processing is a key factor that determines the quality and final application of the finished product.⁶ Ca/Zn stabilizers, especially Ca/Zn stearate, are a type of effective compound used to control the thermal degradation of PVC. Although these stabilizers are more expensive and less effective than many other stabilizer systems, they are widely used in food packaging materials, children's toys and bottle seals because of their physiological harmlessness.⁷ As a result of the stabilizing action, ZnCl₂ is produced in the following reactions (Equations 1 and 2), i.e.,

$$\begin{array}{c} \overset{H}{\overset{}}_{C} \overset{H}{\underset{l}{\overset{}}_{R}} \overset{H}{\underset{l}{}} \overset{H}{\underset{l}{$$

However, the ZnCl₂ formed during these reactions enhances the degradation rate because it acts as a catalyst for the degradation process.⁸ ZnCl₂ causes further rapid degradation. This problem is solved by the synergistic effect of combining alkaline earth (Ca) carboxylates with covalent metal carboxylates or by adding synergistic composite stabilizers, such as phosphate ester and pentaerythritol, to form stable complexes with Zn^{2+} . However, there are still some shortcomings for Ca/Zn stabilizers, such as 'zinc-burning' and inadequate long-term thermal stability. We recently reported⁹ that the pentaerythritol-zinc (Penzinc), which is a novel thermal stabilizer for rigid PVC, can be synthesized through a solid-state reaction. The thermal stability of Penzinc against the degradation of PVC has been evaluated. The oven aging tests indicate that PVC containing Penzinc exhibits clearly enhanced thermal stability. The discoloration time is extended to approximately 90 min. More importantly, no obvious 'zincburning' was observed in the PVC that contained Penzinc. However, the effect of Penzinc on inhibiting the initial color is not sufficient.

In this work, to obtain better initial color and long-term thermal stability, Penzinc was combined with calcium stearate (CaSt₂) or β -diketone. The thermal stabilities of the compounded thermal stabilizers were investigated to determine the most suitable synergistic thermal stabilizer for PVC. Furthermore, we performed quantum chemical calculations using GAUSSIAN 09 to verify the mechanism for the thermal stability of Penzinc.

EXPERIMENTAL PROCEDURE Materials

The PVC (average degree of polymerization: 1005) used in this work was supplied by the China Petrochemical Qilu Limited Company, Zibo, China.

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Table 1 PVC samples compositions used in the experiments (values in phr)

				Additive				
Sample number	PVC	Stearic acid	Penzinc	CaSt ₂	β-diketone			
1	100	1	_	_	_			
2	100	1	4	_	_			
3	100	1	3	1	_			
4	100	1	2	2	_			
5	100	1	1	3	_			
6	100	1	_	4	_			
7	100	1	3	_	1			
8	100	1	2	_	2			
9	100	1	1	_	3			
10	100	1	_	_	4			
11	100	1	2.5	1.2	0.3			

ZnO, pentaerythritol, and the other chemical agents used were all AR grade. Calcium stearate (CaSt₂) and stearoyl benzoyl methane (β -diketone) were kindly supplied by the Huike Additives Company, China.

Synthesis of Penzinc

Approximately 0.51 mol of pentaerythritol and 0.37 mol of ZnO were placed into a mixer at 3000 r min⁻¹ for 5 min. Penzinc was obtained after the homogeneous powder was placed in an oven with a motor stirring at $120 r min^{-1}$ to react at ~210 °C for 2 h. The reaction equation is represented as follows (Equation 3):⁹

$$HO-H_2C CH_2-OH + 2ZnO \longrightarrow Zn CH_2C CH_2-O + 2H_2O - H_2C CH_2-O + 2H_2O - H_2C CH_2-O - H_2C CH_2- H_2C CH_2- H_2C CH_2- H_2C CH_2- H_2C CH_2$$

Sample preparation

The PVC blends were prepared by mixing PVC (powder, 100 phr), stearic acid (powder, 1 phr) and the stabilizers (mixture, 4 phr) in a mixer. The compositions of the samples are listed in Table 1. Fifty-six grams of the PVC blends were milled using an open twin roller at 180 °C for 5 min. The thickness of the drawn-out sheets was 1.0 ± 0.1 mm. Then, the remaining blends were used for the torque rheometry tests.

Measurements

Conductivity measurement: the samples were cut into small squares with dimensions of 0.2×0.2 mm and a total weight of ~ 2 g, and they were subsequently placed into the reaction vessels of a home-made thermal degradation device. The reaction vessels were placed into the heating blocks and heated at 200 °C. Distilled water was placed into the measuring vessels to calculate the change in the conductivity of water.

Thermal aging test: the PVC sheet was cut into small strips $(10 \times 10 \text{ mm})$. These strips were heated in a thermal aging test box at 180 °C and subjected to static thermal aging, according to the ISO standard (Plastics determination of thermal stability of poly(vinyl chloride), related chlorine-containing homopolymers and copolymers and their compounds—discoloration method. ISO 305-1990(E)).

Torque rheometry test: the torque rheometry testing was conducted, according to the ASTM D 2538-79 standard, using a rotor rate of 63 r.p.m. The test temperature was 180 $^\circ C.$

Computational details

PVC is expressed as $(-CH_2-CHCl-)_n$, where *n* denotes the degree of polymerization. A considerable amount of computer memory and a long calculation time period are required to improve the accuracy of the simulation results on the potential energies between two neighboring elements in a PVC



Figure 1 Model samples used in the calculations: (a) 5-carbon vinyl chloride (5C-VC) model molecule; (b) stearoyl benzoyl methane; (c) Penzinc. A full color version of this figure is available at *Polymer Journal* online.

molecule because of its high molecular weight. To reduce the calculation cost and time, a 5-carbon vinyl chloride (5C-VC) molecule (containing an allylic chlorine), which is shown in Figure 1a, was employed as a model molecule. Figure 1b is the model of β -diketone. Although Penzinc is a mixture, Figure 1c is used as the model molecule of Penzinc for computational convenience.

All of the quantum chemical calculations were performed using the GAUSSIAN 09. We used Becke's hybrid three-parameter functional B3LYP with the standard 6–31 G (d) basis set. All of the thermal chemical calculations were performed at 180 $^\circ$ C.

RESULTS AND DISCUSSION

The conductivity test

The thermal degradation of PVC primarily involves the progressive unzipping of neighboring labile chlorine atoms along the polymer chain by heat.¹⁰ When PVC samples are heated in a nitrogen atmosphere, the conductivity of water, through which the nitrogen gas is passed, changes with time. Generally, the rate of the thermal degradation of PVC samples can be evaluated by the change in the conductivity of an aqueous solution because of the HCl gas released during heating. The period from the start of the heating to the point when the conductivity of the solution starts to increase is called the induction time, and the period to the point when the conductivity value reaches $50 \,\mu s \, cm^{-1}$ is called the stability time. This value is the maximum acceptable level of degradation.¹¹ A plot of conductivity vs time for PVC stabilized without or with different amounts of Penzinc, CaSt₂ and β -diketone is shown in Figure 2. In addition, the induction and stability periods are presented in Table 2.



Figure 2 Change of conductivity of an aqueous solution with respect to time at 200 °C for PVC with or without stabilizers. (a) 1, without stabilizers; 2, 4 phr Penzinc. (b) 1, 3 phr Penzinc + 1 phr CaSt₂; 2, 2 phr Penzinc + 2 phr CaSt₂; 3, 1 phr Penzinc + 3 phr CaSt₂; 4, 4 phr CaSt₂ (c) 1, 3 phr Penzinc + 1 phr β-diketone; 2, 2 phr Penzinc + 2 phr β-diketone; 3, 1 phr Penzinc + 3 phr β-diketone; 4, 4 phr β-diketone. A full color version of this figure is available at *Polymer Journal* online.

Figure 2a reveals that the PVC sample stabilized with 4 phr Penzinc presents the longest induction time (87 min) compared with the others at 200 °C because of the highly efficient neutralization of the produced HCl by Penzinc. This sample also has the highest stability time (96 min), as shown in Table 2. A possible mechanism for the stabilizing effect of the Penzinc, on the basis of aforementioned results, implies that the Penzinc that reacts with the released HCl may form a complex-like structure (II) (see Equation 4). Therefore, the ability of Penzinc to neutralize the produced HCl is considerably greater than ZnSt₂ and CaSt₂.

$$\begin{array}{c} O - H_2 C & C H_2 - O \\ Z_n & C - H_2 C & C H_2 - O \end{array} \\ O - H_2 C & C H_2 - O \end{array} + 4HCl \longrightarrow \begin{array}{c} C I & HO - H_2 C & C H_2 - O H \\ C I & HO - H_2 C & C H_2 - O H \end{array}$$

Table 2 Induction, stabilization time values at 200 °C for PVC samples stabilized with Penzinc, Cast₂ and β -diketone

Additive shares				
Penzinc, phr	CaSt ₂ , phr	β-diketone, phr	Induction time (min)	Stabilization time (min)
	_	_	10	24
4	_	_	87	96
3	1	_	62	68
2	2	_	76	81
1	3	_	55	63
_	4	_	34	39
3	_	1	16.5	20
2	_	2	16	18
1	_	3	7.5	12.5
—	_	4	6	8



Figure 3 Change of conductivity of an aqueous solution with respect to time at 180 °C for PVC with 4 phr stabilizers (3 phr Penzinc + 1 phr β -diketone).

When Penzinc is combined with $CaSt_2$, as shown in Figure 2b, both the introduction time and the stability time of the mixed stabilizers are lower than that of pure Penzinc. When the ratio of Penzinc and $CaSt_2$ is 2:2, a relatively long thermal stability time is obtained. This result indicates that there is a weak synergistic effect between Penzinc and $CaSt_2$.

Figure 2c shows the change in the conductivity of the aqueous solution vs time at 200 °C for PVC stabilized with Penzinc and β -diketone. From Figure 2c and Table 2, it can be observed that the induction time and the stability time of the mixed stabilizers with different proportion of Penzinc and β -diketone are all considerably lower than those of pure Penzinc. These results confirm that the long-term thermal stability at 200 °C of Penzinc combined with β -diketone is less effective. However, considering the excellent initial color, the conductivity test of the formulations containing Penzinc and β -diketone (with phr ratio 3:1) at 180 °C was conducted (Figure 3). The induction time extends to 35 min and the stability time increases to 80 min. This result indicates that the synergetic thermal stabilizing effect of Penzinc and β -diketone is excellent at relatively low temperatures, such as 180 °C.

Figures 2 and 3 also show that the time (ΔT) between the induction time and the stability time of the PVC samples are quite different. General speaking, when ΔT is larger, the thermal stability of the PVC samples is better. As for the zinc soap thermal stabilizers, the value of ΔT is very low because the product, ZnCl₂, accelerates the

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Stabilizers		Degradation time, ×10 min								
Formulation	Ratio	0	1	2.5	4	5.5	7	8.5	10	11.5
Pure PVC							-			
Penzinc	4									
	3/1									
Ponzing/CaSt	2/2									
Penzinc/Ca3i ₂	1/3									
	0/4			2.2						
	3/1									
Denzing/// dilustens	2/2									
Penzinc/p-aiketone	1/3									
	0/4									
Penzinc/CaSt ₂ /β-diketone	2.5/1.2/0.3									

Figure 4 Color evolution as a function of time of PVC samples heated at 180 °C. A full color version of this figure is available at Polymer Journal online.

dehydrochlorination after its concentration reaches a certain level. Figure 2 shows that the ΔT values for several stabilizers are very low (only approximately 2–9 min). In other words, although the stabilization time of these stabilizers are sufficiently long, when PVC that contains these stabilizers begins to dehydrochlorinate, these stabilizers would rapidly lose their effectiveness. Figure 3 shows that the ΔT of Penzinc used together with β -diketone in a ratio of 3:1 at 180 °C is quite long. This result indicates that the combination of Penzinc and β -diketone has good thermal stability at 180 °C, and it also demonstrates that there is not a 'zinc-burning' phenomenon for the combination of Penzinc and β -diketone.

The thermal aging test

To conduct the static thermal aging tests by observing the color change of the samples, PVC strips with different stabilizers were heated in a thermal aging test box at $180 \,^{\circ}$ C. Figure 4 shows the color of the samples that were heated at $180 \,^{\circ}$ C for different periods of time.

Figure 4 shows that the color of the PVC strips that contain only Penzinc began to change at 25 min, and they did not turn black until 115 min. Therefore, Penzinc is a thermal stabilizer that not only has a good initial color but also long-term thermal stability. The color of the PVC strips that contained only CaSt₂ began to change even during the milling process with the open twin roller at 180 °C. The PVC strips stabilized with Penzinc and a small amount of CaSt₂ (with phr ratio 3:1) have slightly better resistance to coloration than the PVC strips stabilized with only Penzinc over the same period. The thermal stability of the PVC strips was also observed to worsen with the decreasing Penzinc/CaSt₂ ratio. The results indicate that there is some synergism between Penzinc and CaSt₂, which has an excellent synergistic effect on the thermal stability of PVC.^{12,13} β-diketones are the most popular compounds for providing very good initial color to PVC. These compounds actually accelerate the degradation time owing to their mechanism of action, and they must be used with a good HCl acceptor.¹⁴ The previous results demonstrated that Penzinc is an excellent long-term thermal stabilizer. Therefore, β-diketone should be a good co-stabilizer for Penzinc. The results from the thermal aging test also confirm this conclusion. As shown in Figure 4, the PVC strips that contained Penzinc/β-diketone had the best initial color. When the Penzinc/βdiketone phr ratio is 3:1, perfect thermal stability of the PVC strips can be obtained. The color of the PVC strips does not obviously change during the first 115 min. The thermal stability of the PVC strips worsened with the decreasing Penzinc/β-diketone ratio. The color of the PVC strips that only contained β-diketone began to change at 25 min and became completely black after only 40 min.

Figure 4 also shows that when Penzinc is compounded together with $CaSt_2$ and β -diketone in a 2.5/1.2/0.3 phr ratio for use as a stabilizer for PVC, the PVC strip with the stabilizer mixture has an excellent initial color, color thermal stability and long-term thermal stability.

To determine how long several of the well-behaved formulations are thermally stable, the color evolution as a function of time when the PVC samples were heated at 180°C was monitored until the PVC strips became completely black. The results from this measurement are illustrated in Figure 5. The thermal stability of PVC is defined by the time required for the formation of black decomposition products.¹⁵ As shown in Figure 5, the PVC strips stabilized with only Penzinc and those stabilized with Penzinc/CaSst₂/ β -diketone became completely black after 4.5 h. The thermal stability times of both formulations with Penzinc/CaSt₂ (phr ratio 3:1) and Penzinc/ β diketone (phr ratio 3:1) reach 4 h. These results indicate that both Penzinc or Penzinc combined with CaSt₂ and β -diketone have

Stabilizers			Degradation time, h								
Formulation	Ratio	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Penzinc	4		1								
Penzinc/CaSt ₂	3/1							14. 14.			
Penzinc/β-diketone	3/1								the second		
Penzinc/CaSt ₂ /β-diketone	2.5/1.2/0.3										

Figure 5 Color evolution as a function of time of PVC samples heated at 180 °C. A full color version of this figure is available at Polymer Journal online.



Figure 6 The torque-time curves of PVC, stabilized with different formulations. (a) 4 phr Penzinc. (b) 1, 3 phr Penzinc + 1 phr CaSt₂; 2, 2 phr Penzinc + 2 phr CaSt₂; 3, 1 phr Penzinc + 3 phr CaSt₂. (c) 1, 3 phr Penzinc + 1 phr β -diketone; 2, 2 phr Penzinc + 2 phr β -diketone; 3, 1 phr Penzinc + 3 phr β -diketone. (d) 2.5 phr Penzinc + 1.2 phr CaSt₂ + 0.3 phr β -diketone. A full color version of this figure is available at *Polymer Journal* online.

preferable long-term thermal stabilities. In addition, in the case of the color thermal stability, the PVC strips that contained Penzinc/ β -diketone (phr ratio 3:1) show an obvious improvement, and their color does not change within 2 h and becomes completely black after 4 h at 180 °C.

Torque rheological experiments

The torque-time curves can be obtained from the torque rheological experiments, which can help us study the rheological behavior and the dynamic thermal stability of PVC. A typical torque vs time curve has a sharp loading peak in the first stage. In the second stage, the torque decays and reaches an equilibrium value, which is called the balance torque. The minimum torque is designated as T_{min} , Nm; the maximum torque is designated as T_{max} , Nm.

Figure 6 presents the torque-time curves for PVC that contained different stabilizers. The maxima in torque (T_{max}) , time (t_{max}) and torque at balance (T_e) of the PVC samples are shown in Table 3. From Figure 6 and Table 3, we can see that the PVC that only contains Penzinc has a moderate plasticizing time, a low T_{max} and balanced

torque. The addition of $CaSt_2$ to Penzinc increases the T_{max} and T_e , but it decreases the plasticizing time. When the phr ratio of $CaSt_2$ in the formulations increases, the plasticizing time gradually decreases. The above behaviors suggest that $CaSt_2$ has a certain role in promoting the plastics.

The addition of β -diketone extends the plasticizing time; furthermore, higher ratios of β -diketone result in longer plasticizing times. As shown in Figure 6d, the formulation of Penzinc/CaSt₂/ β -diketone can result in an acceptable plasticizing time.

The results from the computational simulation

It is generally accepted that the thermal dehydrochlorination of allylic chlorides proceeds through an ionic or quasi-ionic manner.¹⁶ The ionic mechanism is depicted in Equation 5, where intermediate III is best regarded as an ion-pair instead of free ions. The quasi-ionic mechanism is shown in Equation 6. Which manner will the thermal dehydrochlorination of the allylic chlorides be in when β -diketone and Penzinc exist? In this paper, the density functional theory method is used to calculate the electron density of PVC, β -diketone and

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Penzinc to help us understand the thermal mechanism.



Figure 7 is the image of the electron density for the model of PVC with allyl chloride (a), model of β -diketone (b), Penzinc (c) and HCl (d), obtained in the computational simulation. The more red an area is, the higher the electron density; the more blue an area is, the lower the electron density. Figure 7a shows that there is high electron density on the allylic chlorine of the 5C-VC, which is expected to show high activity, that is, nucleophilic behavior. It is easy for allylic chlorine to react with the adjacent hydrogen atom whose electron density is low. Figure 7b indicates that the α -H of β -diketone has considerably less electron density. Therefore, the allylic chlorine will preferentially attack the α -H of β -diketone when β -diketone is added to the thermal stabilizer. The mechanism (depicted in Equation 7) involves the concerted loss of HCl in a single step, via a four-center transition state with a large amount of charge separation in breaking C-Cl bond. As a result of the lowest electron density (see Figure 7c), the zinc atoms in Penzinc have a considerable tendency to undergo an electrophilic reaction with the allylic chlorine. The detailed mechanism is depicted in Equation 8. The usage of β -diketone and Penzinc can avoid the formation of conjugated polyene sequences. The difference between β-diketone and Penzinc is that β-diketone will lead to the production of a significant amount of HCl; in other words, β-diketone actually accelerates the degradation because their mechanism of action must be used with a good HCl acceptor.¹⁴ As for Penzinc, although it can also accelerate the remove of allylic chlorine, it will not produce hydrogen chloride. Therefore, the initial color of the PVC stabilized with Penzinc should be better than that stabilized with β -diketone. However, the actual effect is not better. A possible reason is that Penzinc is in a solid state at the processing temperature,

Table 3 Torque rheometer date of PVC containing different stabilizers

Stabilize	ers			
		t _{max} ,	T _{max} ,	T _e ,
		Time of plasticiz	ing	Torque at balance
Formulation	Ratio	(s)	(N m)	(N m)
Penzinc	4	98	18.4	15.2
Penzinc/CaSt ₂	3/1	80	28.3	21.8
	2/2	64	29.3	22.0
	1/3	59	29.3	21.4
Penzinc/	3/1	100	26.0	21.0
β-diketone	2/2	117	21.6	19.7
	1/3	126	17.0	15.0
Penzinc/CaSt ₂ /β-	2.5/1.2/	81	26.1	20.4
diketone	0.3			

which significantly reduces its function.



Figure 7d, which is the model of HCl, shows that the electron density of the hydrogen atom is very low. The oxygen atoms of Penzinc, which have a high electron density, have a tendency to undergo an electrophilic reaction with the hydrogen atom of HCl. Subsequently, the H-Cl bond breaks, and the chloride anion is produced. The chloride anion attacks the zinc atom of Penzinc, which has low electron density, and compound VI in Equation (9) is formed. Equation 9 depicts the reaction mechanism of Penzinc and HCl. If there is sufficient HCl, compound VII in Equation (7) will finally be formed.



The thermal stabilizing mechanism of Penzinc

On the basis of above experimental results, Penzinc is an efficient thermal stabilizer for PVC, which has good initial color and long-term thermal stability, and does not exhibit 'zinc-burning' phenomenon. According to Equations 4 and 9, the ability of Penzinc to neutralize the produced HCl is four-times greater than that of the same amount of ZnSt₂ or CaSt₂, which is the possible reason why Penzinc has such

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Figure 7 The image of the electron density for model of PVC with allyl chloride (a) model of PVC-free radical (b) model of stearoylbenzoylmethane (c) and Penzinc (d). The more *red* an area is, the higher the electron density and the more *blue* an area is, the lower the electron density. A full color version of this figure is available at *Polymer Journal* online.

good long-term thermal stability. Furthermore, the PVC strips that only contain Penzinc have good initial color, and their color does not change during the first 10 min when heated at 180 °C. It is possible that Penzinc can react with the labile chlorine atom in the PVC molecular chain. In our opinion, similar to the fatty acid salt of zinc, Penzinc reacts with PVC by the displacement of labile chlorine atoms (Equation 8) to form a more stable structure (V).

Usually, the addition of the β -diketone as a co-stabilizer to the primary stabilizer system of ZnSt₂/CaSt₂ for PVC improves the initial color. It has been shown that β -diketone can substitute the labile chlorine atoms through a C-alkylation reaction.¹⁷ These compounds actually accelerate the degradation process owing to their mechanism of action and must be used with a good HCl acceptor.¹⁴ Considering the excellent ability of Penzinc to absorb HCl, there would be a wonderful synergistic effect between Penzinc and β -diketone. The above results also demonstrated that β -diketone is the most efficient synergistic co-stabilizer of Penzinc.

CONCLUSIONS

Penzinc can prevent the early discoloration of resin. Therefore, this compound can most likely react with labile chlorine atoms in PVC chains. The long-term thermal stability measurements indicate that Penzinc can easily react with the HCl generated through the degradation process. Penzinc possesses the two basic functions required of the thermal stabilizers for PVC.¹⁸ Therefore, Penzinc is an efficient thermal stabilizer for PVC compared with the commonly used reference stabilizers, such as Ca-Zn soap.

CaSt₂ reduces the thermal stability time of PVC when used together with Penzinc, which demonstrated that there is a weak synergistic effect between Penzinc and CaSt₂.

Compared with Penzinc, β -diketone cannot delay the degradation of PVC, but it can remarkably improve the color thermal stability of PVC. The formulation of Penzinc/ β -diketone (phr ratio is 3:1) is the most active thermal stabilizer.

The results from the computational simulation reveal the different electron densities of PVC that contains allyl chloride, β -diketone and Penzinc. The results indicate that both the α -H atom of β -diketone and the zinc atom of Penzinc, which have low electron densities, can easily react with the labile chloride atom of PVC, which has a high electron density. The difference between β -diketone and Penzinc is that the reaction between β -diketone and the labile chloride can produce HCl, whereas the reaction with Penzinc can not.

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