

Tin Dioxide Coated Calcium Carbonate as Flame Retardant for Semirigid Poly(vinyl chloride)

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ABSTRACT: The flame retardant and smoke suppressant properties of semirigid PVC treated with calcium carbonate (CaCO_3), tin oxide (SnO_2), the mixture of $\text{CaCO}_3/\text{SnO}_2$ and SnO_2 -coated CaCO_3 have been studied through the limiting oxygen index, char yield, and smoke density rating (SDR) methods. The thermal degradation in air of the treated semirigid PVC was studied by thermogravimetry (TG) and differential thermal analysis (DTA) from ambient temperature to 1073 K. The morphologies of the additives and the char formation were studied through SEM. The mechanical property was also studied. The results showed that the semirigid PVC treated with SnO_2 -coated CaCO_3 has a higher limiting

oxygen index and char yield, lower SDR and MSDR, a more compact structure of char formation than the semirigid PVC without flame retardant and the semirigid PVC with the equivalent CaCO_3 , or SnO_2 , or the mixture of $\text{CaCO}_3/\text{SnO}_2$, a similar tensile property and greatly improved impact strength compared with that of the semirigid PVC without flame retardant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 731–738, 2006

Key words: degradation; flame retardance; poly(vinyl chloride); thermal properties; tin oxide

INTRODUCTION

Poly(vinyl chloride) (PVC) is inherently fire retardant and smoke retardant, and its performance is acceptable for certain applications because of its higher chlorine content. But when PVC is plasticized by DOP [di(2-ethylhexyl) phthalate], its fire performance is less favorable and there will be a potential danger to people's life and riches.

To overcome the potential hazard a number of flame retardants are used. Compared with other plastic additives, the two main basic rules for the selection of flame retardant is that (1) it meets minimum performance requirements at the least possible raw material and processing costs, (2) and there should be concerns for nontoxicity and environmental safety.¹ To meet the requirement of reducing the processing costs, many relatively low cost inorganic compounds are added into the PVC resins. Some of the inorganic compounds are active, while the others are inert. As a cheap, rich reserve and typical inert filler used for PVC, calcium carbonate (CaCO_3) was selected as the material of improving the processing character of PVC in this study. To meet the requirement of good flame retardance, smoke suppression, nontoxicity, and environmental friendly, the inorganic tin compounds have been receiving increasing attention in recent years.^{2–6}

For example, tin compounds such as zinc hydroxystannate (ZHS), zinc stannate (ZS) and tin oxide (SnO_2) have been shown to have good flame-retardant and smoke-suppressant properties in halogen-containing polymer such as PVC, neoprene and hypalon.⁶ Hydrated stannic oxide has been found to be at least equally as effective as antimony oxide (Sb_2O_3) in model plastic systems.⁷ Bearing in mind that Sb_2O_3 is used in many polymer systems,² this warrants the further attention of SnO_2 .

One of the main research objects is to make the flame retardant and smoke suppressant properties of SnO_2 more effective and highly usable at a much lower cost. In this paper, SnO_2 -coated (10%) CaCO_3 was prepared and applied for the treatment of semirigid PVC, and the flame retardant and smoke suppressant properties of it was compared with that of CaCO_3 , SnO_2 , and a mixture of $\text{CaCO}_3/\text{SnO}_2$ (9 : 1), respectively.

EXPERIMENTAL

Materials

The materials used were PVC SG-3 (Beijing Second Chemical, Beijing), DOP [di(2-ethylhexyl) phthalate] as plasticizer (Shanghai Dongfang Chemicals, Shanghai), organic tin compound as stabilizer and calcium stearate as lubricant (Hebei Baoding Chemical, Baoding City). CaCO_3 (Shanghai Yexing Pesticide Chemical, Shanghai), $\text{Na}_2\text{Sn}(\text{OH})_6$ (Tianjin Suzhuang Chem-

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ical, Tianjin), urea (Tianjin Chemical, Tianjin), and SnO₂ (Beijing Chemical, Beijing) were also used.

Preparation of flame-retardants and PVC samples

The preparation of flame-retardant SnO₂-coated CaCO₃ was according to the method mentioned in Ref. 6. Thirty grams of calcium carbonate was slurried by rapid stirring in 300 mL of an aqueous solution containing 4.4 g sodium hydroxystannate and 10 g urea. The slurry was heated to 358 K and maintained at that temperature for 8 h. After the reaction mixture had been allowed to cool to room temperature, the solid product was separated from the solution by filtration, washed three times with distilled water, and dried in air at 383 K. The dried cake was crushed in a mortar and pestled to give 33.2 g (98% yields) of a fine white powder. This product (SnO₂-coated CaCO₃ analyzed to a composition of 9.64% SnO₂ + 91.36% CaCO₃, was equivalent to a coating level of 10.67% w/w on the filler.

Semirigid PVC samples were prepared by mixing PVC with DOP, heat stabilizer, lubricant, coupling agent, and the selected flame retardant, then blending them in a two-roll mill at 443 K for 10 min and compressing them at 453 K to form sheets of 100 × 50 × 3 mm³. Different shapes, sizes, and forms of semirigid PVC samples were prepared using appropriated molds, the samples for analysis being ground before use.

The basic recipe of the samples is as follows: sample I, PVC 100 parts, DOP 30 parts, stabilizer 3 parts, calcium stearate 0.5 parts, stearic acid 0.5 parts, and coupling agent 1 part; the other samples containing the materials of sample I and some flame retardants.

Measurements and characterization

Although the oxygen index test (LOI; ASTM D2863/ISO 4589-2) is not applicable to real fires, it is indicative of low applied heat ease of extinction, and is widely used for specifications.⁷ The LOI value is the minimum amount of oxygen in oxygen–nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. In this research, the LOI values were determined in accordance with ASTM D2863 by means of a general model HC-1 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing).

Char yield values were calculated by the following equation:

$$\text{Char yield} = w_2/w_1 \times 100\%$$

where w_1 and w_2 were the weight of PVC samples before pyrolysis under N₂ and the residue after pyrolysis of the PVC samples, respectively. This experiment

was carried out in a muffle furnace under N₂ at 673 K for 30 min.

Smoke density rating (SDR) was determined using the JCY-1 instrument (Nanjing Analysis Instrument Factory, Nanjing) according to ASTM D 2843 method, and the size of the test specimens was 25.3 × 25.3 × 3 mm³.

Thermal analysis has been widely used for the measurement and comparison of the stages of degradation of the additives alone, of the resin alone and of the additives-containing resins. The thermal stability of the resins may be assessed by the temperature range of their mass losses measured by TG, while the effects of additives on the heat changes during decomposition can be studied by DTA and were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). TG and DTA were performed under air at a heating rate of 10 K min⁻¹ and an air flow rate of 60 mL min⁻¹, α-Al₂O₃ was taken as the reference material. The temperature range was from room temperature to 1073 K.

The morphology of the additives and the char formed after heating of the samples was investigated by means of scanning electron microscopy (SEM-KYKY-2800B, Chinese Academy of Science Instrument Factory, Beijing). The surfaces of the char were covered with gold before observation.

The tensile strength and elongation measurements were carried out on LJ-5000N mechanical instrument (Chengde Experimental Instrument Factory, Chengde) according to ISO: 10,810 method.

The impact strength measurement was carried out on X CJ-40 Charpy impact test machine (Chengde Experimental Instrument Factory, Chengde) according to ISO:179 method.

RESULTS AND DISCUSSION

Flame retardant and smoke suppressant properties

The observed LOI of the semirigid PVC samples are shown in Figure 1, the char yields are shown in Figure 2, and the smoke suppressant properties are described in Table I.

In general, as shown in Figure 1, the LOI was improved along with the increasing content of the additives except CaCO₃. At the same additive level, the flame retardant properties of SnO₂-coated CaCO₃ was the best among the three kinds of additives (SnO₂-coated CaCO₃, the mixture of CaCO₃/SnO₂ and CaCO₃), and that of CaCO₃ was the worst; at the same content of the effective flame retardant SnO₂, the flame retardant effect of SnO₂-coated CaCO₃ was better than that of SnO₂ or the mixture of CaCO₃/SnO₂, and that the flame retardant effect of most of the SnO₂ was better than that of the mixture of CaCO₃/SnO₂, except for the equal effect. For example, when 10 parts of additives was added, the LOI of sample D (the semi-

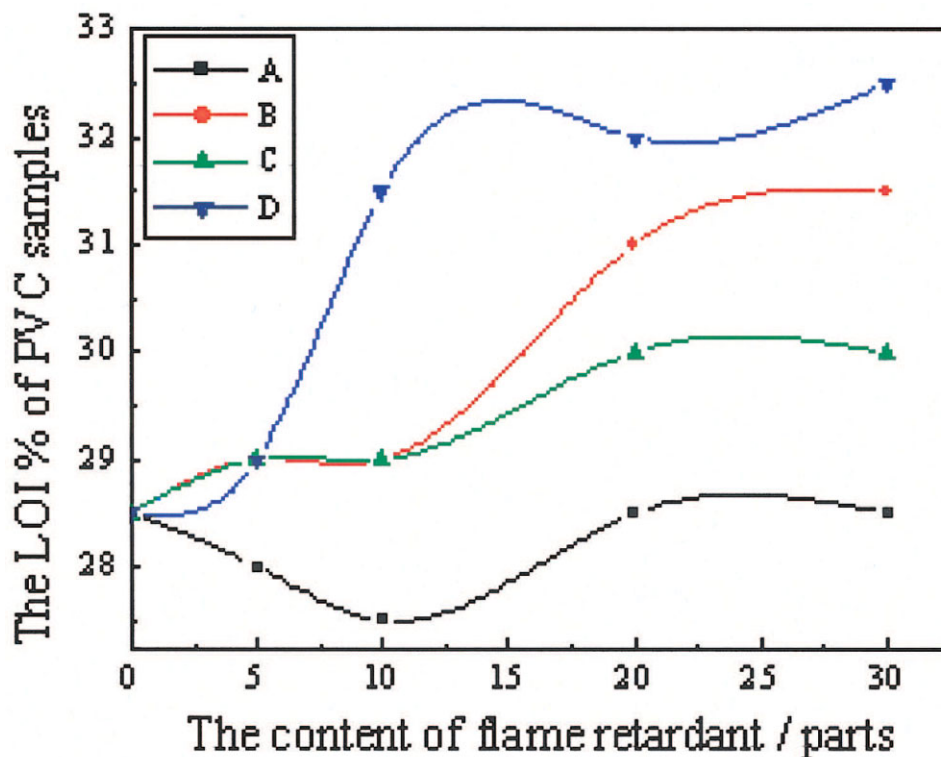


Figure 1 The LOI of the PVC samples. A–D are the PVC samples containing CaCO₃, SnO₂, CaCO₃/SnO₂ (9:1), and SnO₂-coated CaCO₃, respectively. The contents of A, C, and D are the same as that shown in the figure, and the content of B is one tenth as that shown in the figure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rigid PVC sample containing SnO₂-coated CaCO₃) was 2.5 units higher than that of sample C (the semirigid PVC sample containing the mixture of CaCO₃/SnO₂), 4 units higher than that of sample A (the semirigid PVC sample containing CaCO₃), and 3 units higher than the semirigid PVC without flame retardant additives. When 1.0 parts of the effective flame retardant SnO₂ (the third dot in the curve as shown in Fig. 1) was added, the LOI of sample D was 2.5 units higher than that of sample C or sample A; and when the content of SnO₂ was increased the LOI of sample D was the highest, and that of sample C was the lowest. These indicated that SnO₂, SnO₂-coated CaCO₃, and the mixture of CaCO₃/SnO₂ are effective flame retardants for semirigid PVC, and SnO₂-coated CaCO₃ has the best effect at the same effective additive level; CaCO₃ has little or no flame retardant effect on semirigid PVC, and it is only an inert filler.

As shown in Figure 2, when ten or over ten parts of the additives was added, the char yield of sample D was the highest among the three kind of samples (sample A, sample C, and sample D), and this was consistent with its highest LOI among the three kind of samples; and that of sample C was higher than that of sample A except adding 30 parts of additives. When 1.0 or over 1.0 parts of the effective flame retardant

SnO₂ were added, the char yield of sample D was the highest among the three kind of samples (sample B, sample C, and sample D), and this was consistent with its highest LOI among the three kind of samples; and that of sample B was nearly the same as that of sample C, except 16 units lower than the latter when 3.0 parts of additives were added, which was different from the LOI character of them. For example, when 10 parts of additives were added, the char yield of sample D (25.51%) was 3.6–5.4 units higher than that of sample C (21.41%), sample A (21.41%) and the semirigid PVC without flame retardant additives; when the additive level was increased to 30 parts, that of sample D was 41.78 and nearly the same as that of sample C (41.20), 4 units higher than sample A, and 20 units higher than the semirigid PVC without flame retardant additives. When 1.0 parts of the effective flame retardant SnO₂ was added, the char yield of sample D was the highest among the three kind of samples (sample B, sample C, and sample D); and when the content of SnO₂ was increased to 3.0 parts, that of sample D was 41.78 and nearly the same as that of sample C, and 9.5 units higher than that of sample B. These indicated that CaCO₃, SnO₂, the mixture of CaCO₃/SnO₂, and SnO₂-coated CaCO₃ can greatly increase the char yield of

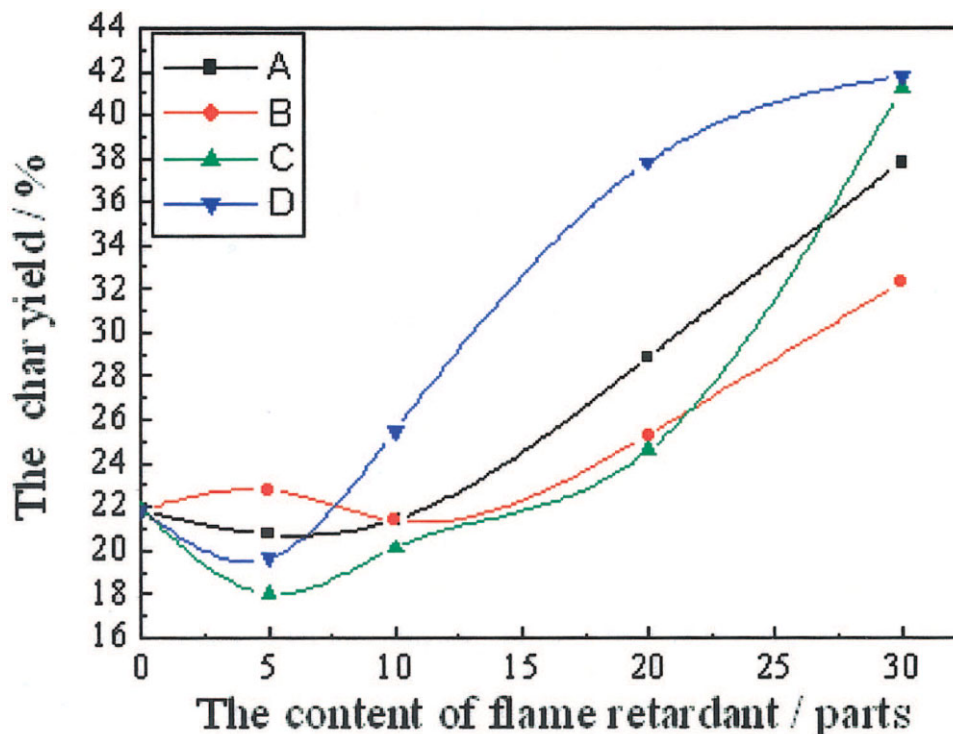


Figure 2 The char yield of the PVC samples. A–D are the PVC samples containing CaCO_3 , SnO_2 , $\text{CaCO}_3/\text{SnO}_2$ (9:1), and SnO_2 -coated CaCO_3 , respectively. The contents of A, C, and D are the same as that shown in the figure, and the content of B is one tenth as that shown in the figure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

semirigid PVC at a certain additive level, and the effect of SnO_2 -coated CaCO_3 is the most obvious.

To investigate the smoke suppressant properties of CaCO_3 , SnO_2 , the mixture of $\text{CaCO}_3/\text{SnO}_2$, and SnO_2 -coated CaCO_3 on the semirigid PVC, the samples containing 10 parts (or 1.0 parts of SnO_2) of additives were selected as the study objects (as shown in Table I). As shown in Table I, the SDR and MSDR were decreased along with the order of sample (a)–sample (e) which indicated that the smoke suppressant properties of SnO_2 -coated CaCO_3 was the best among the given additives mentioned in Table I. The SDR of sample (b)

and sample (c) was 85.54% and 82.31%, respectively. It was 3.59% and 6.82% lower than the semirigid PVC (sample (a)) and 10 and 8 units higher than the standard (75%). The SDR of sample (d) and sample (e) was 18.43% and 21.07% lower than sample (a), 4.3 and 6.94 units lower than the standard, respectively. These indicated that the addition of CaCO_3 or SnO_2 separately can decrease the production of smoke, but it cannot meet the requirement of application. The addition of the mixture of $\text{CaCO}_3/\text{SnO}_2$ or SnO_2 -coated CaCO_3 can greatly decrease the production of smoke and meet the requirement of application, but the effect of the latter is better than that of the former.

All in all, SnO_2 -coated CaCO_3 has highly effective flame retardant and smoke retardant properties on semirigid PVC.

TABLE I

The Smoke Suppressant Properties of the PVC Samples

Sample	SDR (%)	MSDR (%)
a	89.13	100
b	85.54	97.42
c	82.31	97.06
d	70.70	88.96
e	68.06	83.77

a, Sample I (the semi-rigid PVC without flame retardant additives); b, Sample I + CaCO_3 10 parts; c, Sample I + SnO_2 1.0 parts; d, Sample I + SnO_2 1.0 parts + CaCO_3 9 parts; e, Sample I + SnO_2 coated CaCO_3 10 parts.

Thermal properties analysis

Figure 3 shows the TG and DTA curves of the semirigid PVC samples with and without flame retardants, and Table II describes the parameters of the corresponding samples. As shown in Figure 3, all the additives affect the thermal degradation of the semirigid PVC. The TG curves of the given samples can be divided into two

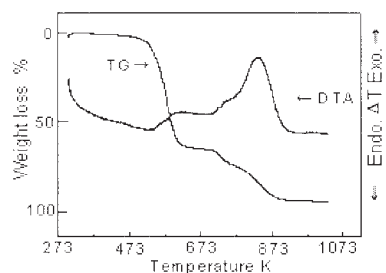


Figure 3 (1) Sample I

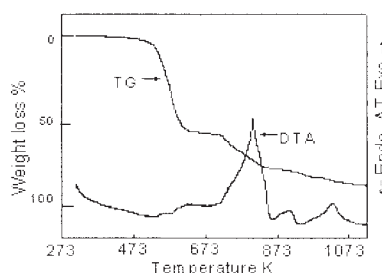
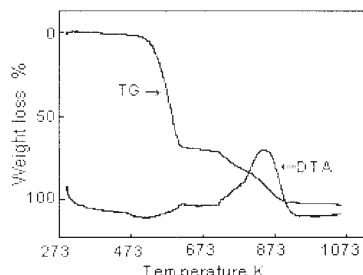
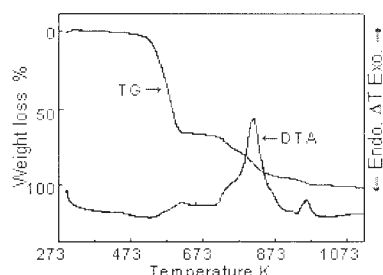
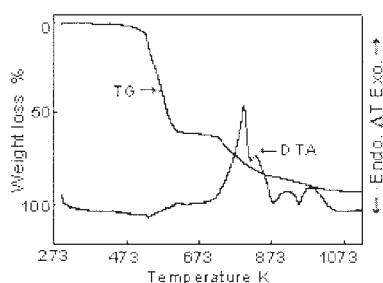
Figure 3 (2) Sample I + CaCO₃ 10 partsFigure 3 (3) Sample I + SnO₂ 1.0 partsFigure 3 (4) Sample I + SnO₂ 1.0 parts + CaCO₃ 9 partsFigure 3 (5) Sample I + SnO₂ coated CaCO₃ 10 parts

Figure 3 (a)–(e) shows the TG and DTA curves of the semirigid PVC samples. (a) sample I, the semirigid PVC without flame retardant additives, (b) sample I + CaCO₃ 10 parts, (c) sample I + SnO₂ 1.0 parts, (d) sample I + SnO₂ 1.0 parts + CaCO₃ 9 parts, (e) sample I + SnO₂-coated CaCO₃ 10 parts.

stages, and weight was lost mainly in the first stage, which can also be seen from Table II. The weight loss was from 50.76% to 69.45% in the first stage and from 27.36% to 32.01% in the second stage. In the first stage, the average weight loss was decreased from 0.37% K⁻¹ to 0.27% K⁻¹ in the order of sample (a)–sample (e). In the second stage, the average weight loss of sample (b)–sample (e) was lower than sample (a) which testified the effect of the additives. The minimum value of the average weight loss was caused by the addition of CaCO₃ (sample (b)); and the average weight loss of sample (e) was the second smallest. The addition of the given additives, except CaCO₃, can decrease the T₁%, which may be caused by the addition of SnO₂. These indicated that SnO₂-coated CaCO₃ can decrease the velocity of decomposability in the whole decomposing process, and outperform equiva-

lent weight mixture of CaCO₃/SnO₂, CaCO₃, or SnO₂, respectively.

As shown in Figure 3 and as described in Table II, a marked difference was observed between the SnO₂-coated CaCO₃ and the equivalent mixture of CaCO₃/SnO₂, CaCO₃ and SnO₂ from the DTA curves. The SnO₂ did not change much of the peak temperature or produce any new peaks, whereas CaCO₃, the mixture of CaCO₃/SnO₂, and SnO₂-coated CaCO₃ produced new peaks. The semirigid PVC sample without additives (sample (a) and the semirigid PVC sample with 1.0 part SnO₂ (sample (c) presented only one of the exothermic peaks at 833 and 841 K, respectively. The semirigid PVC samples containing CaCO₃ (sample (b) sample (d) and sample (e) showed a complex DTA curve respectively. Sample (b) and sample (e) both pre-

TABLE II
The Results of TG and DTA Curves of the Semi-rigid PVC Samples

Sample	T_{exo} (K)	T_{endo} (K)	$T_{1\%}$ (K)	First stage			Second stage		
				(T_1-T_2) (K)	$\Delta m/m$ (%)	AR (% K ⁻¹)	(T_1-T_2) (K)	$\Delta m/m$ (%)	AR (% K ⁻¹)
a	833	—	450	450–622	63.87	0.37	712–902	27.36	0.14
b	803, 903, 1025	—	463	463–631	57.60	0.34	716–1057	28.71	0.08
c	841	—	412	412–622	69.45	0.33	699–938	31.12	0.13
d	813, 962	—	397	397–633	66.21	0.28	693–1001	32.01	0.10
e	795, 913, 979	532	413	413–641	60.93	0.27	706–1029	30.19	0.09

a, Sample I (the semi-rigid PVC without flame retardant additives); b, Sample I + CaCO₃ 10 parts; c, Sample I + SnO₂ 1.0 parts; d, Sample I + SnO₂ 1.0 parts + CaCO₃ 9 parts; e, Sample I + SnO₂ coated CaCO₃ 10 parts; T_{exo} , temperature of exothermic peak; T_{endo} , temperature of endothermic peak; $T_{1\%}$, the temperature at which the samples decomposes by 1%; (T_1-T_2) , temperature range; $\Delta m/m$ %, weight loss; AR = $[(\Delta m/m)\%]/(T_2-T_1)$, the average weight loss.

sented three exothermic peaks, and sample (e) showed one endothermic peak at 532 K; sample (d) showed two exothermic peaks. The significant difference of sample (e) from the others indicated a strong interaction between SnO₂-coated CaCO₃ and PVC resin.

SEM analysis

As shown in Figure 4(a)–4(c), the morphology of the SnO₂-coated CaCO₃ was quite different from that of CaCO₃, but it was more like the morphology of SnO₂. This may be caused by the creation of SnO₂ on the surface of CaCO₃. The morphology of the char formed after heating of semirigid PVC containing the given additives (sample (f)–sample (h) in air was quite different from that of char formed after heating of sample I and the sample containing CaCO₃. As shown in Figure 4, the morphology of the semirigid PVC without additives (sample (a) showed an incompact structure with some small pores; the char surface of the semirigid PVC sample containing CaCO₃ (sample (e) was dotted with solid particles; the char surface of the semirigid PVC sample containing SnO₂ (sample (f) was smooth, and a bumpy and incompact inner-structure could be seen from the split; the char surface of the semirigid PVC sample containing the mixture of CaCO₃/SnO₂ was more compact than sample (d)–sample (f); the char surface of the semirigid PVC sample containing SnO₂-coated CaCO₃ (sample (h)) was the most compact of the five semirigid PVC samples, without any holes, any splits and any inorganic particles dotted on the surface. The compact and continuous char of sample (h) could insulate the rest of the semirigid PVC from heat, exclude oxygen, and slow the rate of diffusion of volatile flammable pyrolysis fragment.

Mechanical properties of the PVC samples

As shown in Table III, the addition of the flame-retardants reduced the tensile strength and elonga-

tion, improved the impact strength of the nonflame retardant PVC sample. When 10 parts SnO₂-coated CaCO₃ was added into the PVC samples (sample (e)), the tensile strength had little difference with that of the untreated PVC sample (sample (a)), and higher than that of the PVC sample containing the other additives (CaCO₃, SnO₂, and the mixture of CaCO₃/SnO₂, (sample (b)–sample (d)). The elongation of sample (e) was lower than that of sample (a) or sample (c) and higher than sample (b) or sample (d); the impact strength (70.67 kJ/m²) was 28.27 and 14.85 times as that of sample (a) (2.50 kJ/m²) and sample (b), respectively, but it was very similar to that of sample (c) (68.52 kJ/m²) or sample (d) (68.79 kJ/m²). These indicated that SnO₂-coated CaCO₃ has little influence on the tensile property of the PVC sample, it can greatly improve the impact strength, and it is a kind of better additive than SnO₂, CaCO₃, and the mixture of CaCO₃/SnO₂ respectively.

Flame retardant mechanism of SnO₂-coated CaCO₃

Tin compounds have been shown to be effective flame retardant synergists and smoke suppressants in several polymer systems. They act as flame retardants by a combination of condensed phase and vapor phase mechanisms and the latter is more halogen dependent.² It has been reported that ZHS-coated and ZS-coated products have effective flame retardancy than uncoated products, which may be caused by an integrated effect of many kinds of flame retardant mechanism, but the mechanism has no definite conclusions.⁸ In this study, SnO₂-coated CaCO₃ was found to be a good flame retardant and smoke suppressant than the equivalent mixture of CaCO₃/SnO₂, CaCO₃ or SnO₂. According to the experimental data and the work of a former study,^{2-5,9} we suggested that the following two reasons explained the increase of flame-retardancy of SnO₂-coated CaCO₃.

The first was the good dispersement of SnO₂ in PVC resin. The process of preparing SnO₂-coated CaCO₃

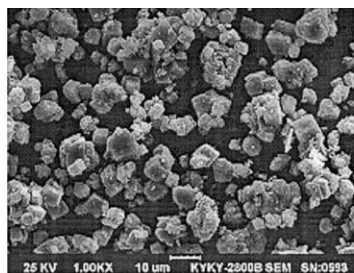
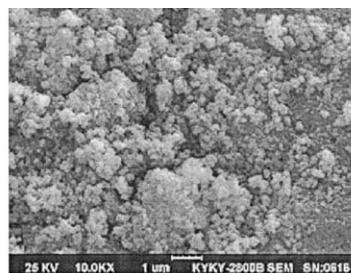
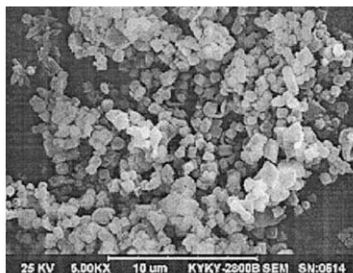
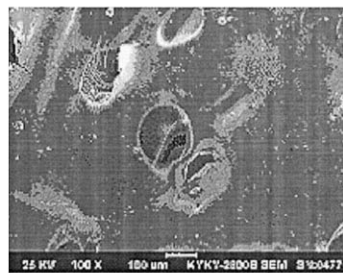
Figure 4 (1) CaCO₃Figure 4 (2) SnO₂Figure 4 (3) SnO₂ Coated CaCO₃

Figure 4 (4) Sample I

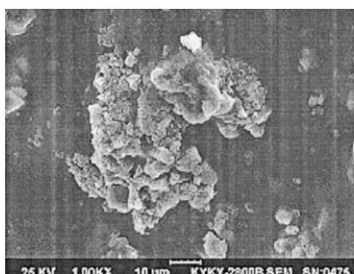
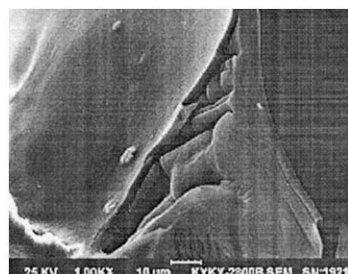
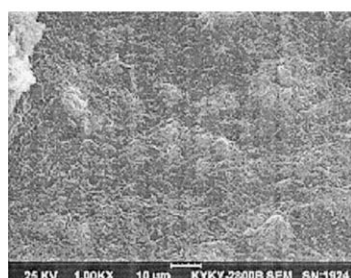
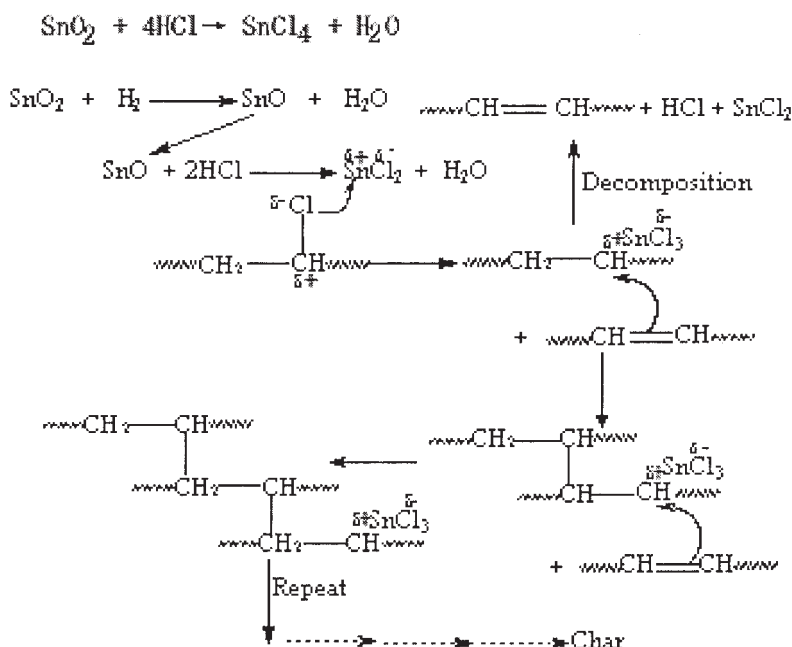
Figure 4 (5) Sample I+CaCO₃ 10 partsFigure 4 (6) Sample I + SnO₂ 1.0 partsFigure 4 (7) Sample I + SnO₂ 1.0 parts+ CaCO₃ 9 partsFigure 4 (8) Sample I + SnO₂ coated CaCO₃ 10 parts

Figure 4 SEM of the additives and the char yield formed after heating of the semirigid PVC samples. (a)–(c) shows the SEM of additives, (a) CaCO₃, (b) SnO₂, (c) SnO₂-coated CaCO₃ (d)–(h) shows the SEM of the char yield formed after heating of the semirigid PVC samples, (d) sample I, the semirigid PVC without flame retardant additives, (e) sample I + CaCO₃ 10 parts, (f) sample I + SnO₂ 1.0 parts, (g) sample I + SnO₂ 1.0 parts + CaCO₃ 9 parts (h) sample I + SnO₂-coated CaCO₃ 10 parts.

made SnO₂ disperse on the surface of CaCO₃ more equably, which made the equivalent SnO₂ disperse in PVC adequately, contact and interact with the PVC resin more easily.

The second was the condensed phase and vapor phase mechanisms of the effective composition SnO₂. One part of the SnO₂ reacted with HCl that was released from PVC when heated to form tin tetrachloride (SnCl₄), which volatilized owing to its low boiling

point 389 K,² and interfered with exothermic free radical propagation reactions in the flame, reduced burn velocity and narrowed flammability limits of the substance. The other part of the SnO₂ was reduced to SnO by H₂, which was produced during the pyrolysis of PVC, and SnO reacted with HCl to form the final product SnCl₂ and H₂O. SnCl₂ (bp 896 K) acted as a kind of Lewis acid in the condensed phase. The flame retardant process of SnO₂ was as follows¹⁰:



The semirigid PVC treated with SnO_2 -coated CaCO_3 formed a more compact and nonflammable char to insulate the rest of the PVC resins from heat, exclude oxygen, and slow the rate of diffusion of volatile flammable pyrolysis fragment (as shown in Fig. 4).

CONCLUSIONS

1. When at the equivalent content of SnO_2 , the flame retardant and smoke suppressant properties of SnO_2 -coated CaCO_3 was better than SnO_2 and the mixture of $\text{CaCO}_3/\text{SnO}_2$, respectively
2. SnO_2 -coated CaCO_3 has little influence on the tensile property of the semirigid PVC samples. It can greatly improve the impact strength, and it is a kind of better flame retardant additives

than SnO_2 , CaCO_3 , and the mixture of $\text{CaCO}_3/\text{SnO}_2$, respectively.

3. The TG results showed that SnO_2 -coated CaCO_3 can decrease the velocity of decomposability in the whole decomposing process and promote char formation. The significant difference of the DTA curve of the semirigid PVC sample containing SnO_2 -coated CaCO_3 from the others indicated a strong interaction between SnO_2 -coated CaCO_3 and PVC resin.
4. The morphology of the char of semirigid PVC treated with SnO_2 -coated CaCO_3 showed a more compact and nonflammable char than that treated with SnO_2 , and the mixture of $\text{CaCO}_3/\text{SnO}_2$.

TABLE III
The Mechanical Properties of the PVC Samples

Sample	Tensile strength (MPa)	Elongation (%)	Impact strength (kJ/m^2)
a	25.79	93.22	2.50
b	23.26	80.27	4.76
c	24.38	90.18	68.52
d	23.85	85.36	68.79
e	25.02	88.96	70.67

a, Sample I; b, Sample I + CaCO_3 10parts; c, Sample I + SnO_2 1.0 parts; d, Sample I + SnO_2 1.0 parts + CaCO_3 9 parts; e, Sample I + SnO_2 coated CaCO_3 10 parts.

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