

Synthesis of Zn_2SnO_4 Using Activated Carbon as Template and Its Flame Retardant Application in Flexible Poly (Vinyl Chloride)

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Abstract—Flame retardant Zn_2SnO_4 were prepared through the method of precursor calcinations with $SnCl_4$, $Zn(NO_3)_2$ and NaOH as raw materials and activated carbon as template. Zn_2SnO_4 as flame-retardants and smoke suppressants for flexible poly (vinyl chloride) were characterized by the limiting oxygen index test (LOI), smoke density test (SDR) and the char yield test. The mechanical properties of modified PVC were also studied. The results showed when 20phr Zn_2SnO_4 was used, PVC showed excellent flame retardant and smoke suppression, LOI, SDR and char yield was 37.9%, 84.5%, 29.8%, respectively, tensile strength was 21.52MPa, elongation was 246%. The thermal degradation of modified PVC were studied by differential thermal analysis, thermogravimetry and scanning electron microscope. The results demonstrated that Zn_2SnO_4 can be used as a highly effective flame retardant for flexible PVC.

Keywords-flame retardant; Zn_2SnO_4 ; activated carbon; poly (vinyl chloride); smoke suppression; thermal analysis

I. INTRODUCTION

Poly (vinyl chloride) (PVC) is a well-known, economical polymer. PVC is inherently fire retardant and smoke retardant and its performances are acceptable for certain applications because of its higher chlorine content. But when PVC is plasticized by DOP (Dioctyl phthalate), its fire performance is less favorable and there will be a potential danger to people's lives and treasures. So it is very crucial to study the flame retardant and smoke suppression PVC.

Zn-Sn-O composites are known as non-toxic flame retardant and smoke suppressant agent for a wide range of organic polymers. Particularly in the polymer which contains organic chlorine compounds good flame retardant have been shown [1-3]. There are two compounds in Zn-Sn-O composites, Zn_2SnO_4 and $ZnSnO_3$. At present, the study of $ZnSnO_3$ flame retardant is relatively wide, on top of that, the application of Zn_2SnO_4 mainly fall into light-emitting materials and conductive materials [4-6]. Research of Zn_2SnO_4 as PVC flame retardant has not yet been reported.

The recently reported carbon template method has been shown to be successful for the synthesis of zeolites, metal and oxides [7-9] with high surface area, which allowed the effective control of the resulting materials by adjusting the conditions of synthesis. Carbon templates are attractive due to their high surface areas, low cost and also because they

can be easily removed by combustion. The route involves two steps: the impregnation of high surface area carbon materials with nitrate or chlorate solutions and burn-off to remove the carbon materials in a controlled oxidation atmosphere.

In this work, face-centered cubic Zn_2SnO_4 were prepared with or without activated carbon material as template. The purpose of our present study is to compare the flame-retardant, smoke-suppression and mechanical properties of PVC samples that are treated with different Zn_2SnO_4 .

II. EXPERIMENTAL

A. Materials

The materials used were PVC TL-1000 (Tianjin Lejin Dagu Chemical Co., Tianjin, China); DOP as the plasticizer (Shanghai Dongfang Chemicals Co., Shanghai, China); organic tin compound as stabilizer and calcium stearate as lubricant (Hebei Baoding Chemicals Co., Baoding City, China); Activated carbon material as template (Norit Trading (Shanghai) Co., Netherlands). NaOH, $SnCl_4$, and $Zn(NO_3)_2$ as agents (Tianjin Kemiou Chemical Co., Tianjin, China) for the preparation of Zn_2SnO_4 .

B. Preparation of Flame Retardants and PVC Samples

The preparation of flame retardants Zn_2SnO_4 was as follows [10]: Dried activated carbon was impregnated by an aqueous saturated $Zn(NO_3)_2/SnCl_4$ (Zn: Sn; 2: 1) solution and then added drop-wise to another aqueous solution (100mL) containing 16g of NaOH in rapid stirring at room temperature. The dropping was finished when the pH reached to 9 to 10 while the stirring continued for 1 hour. Then, the solid product was separated from the solution by filtration, finally the product were washed with distilled water until the pH reached to 7, and dried at 80 °C for 1 h. The impregnated carbon was then calcined (1 h at 850 °C, rate 5 °C/min).

Samples were prepared by mixing PVC with DOP, heat stabilizer, lubricant, coupling agent and a certain of flame retardants, then they were blended in a two-roller at 170 °C for 10 min and compressed at 180 °C to form sheets of 100 mm × 50 mm × 6 mm. The test specimens were cut from the molded sheets. The based recipe for all of the samples is as follows: PVC 100 g, DOP 30 g, stabilizer 3g, calcium stearate 0.5 g, stearic acid 0.5 g, coupling agent 1g and

some flame retardants.

C. Measurements and Characterization

The products were characterized by X-ray diffraction (XRD) in reflection mode (Cu K_{α} radiation) on a Bruker D8 diffractometer. Scans were recorded with a scanning rate of 0.01 $^{\circ}$ /sec, typically in the angle range between 10 $^{\circ}$ and 90 $^{\circ}$.

The limiting oxygen index (LOI) value is the minimum amount of oxygen in an oxygen/nitrogen mixture that is required to support complete combustion of a vertically held sample burned down ward from the top. The higher the LOI value is, the more effective the flame-retardant treatment is. The LOI values were determined in accordance with ASTM D2863-2000 by means of a General Model HC-1 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China).

The smoke density rating (SDR) and the maximum smoke density (MSD) evaluations of the samples, in the form of plates measured 25mm \times 25mm \times 3mm, were determined in accordance with ASTM D2843-1993 by means of a General Model JCY-1 instrument (Nanjing Jiangning Analysis Instrument Factory). The method is to measure the light absorption rate of the smoke during the initial period of the 4-min period of burning time. A special smoke chamber made of heat insulated material was used. The chamber was equipped with an ignition system, an illuminance measuring system and a ventilation system.

The char yield values were calculated as $w_2/w_1 \times 100\%$, where w_1 and w_2 are the weights of PVC samples before combustion and of the residue after combustion, respectively. This experiment was carried out in a muffle furnace under N_2 at 400 $^{\circ}C$ for 40 min.

The tensile strength and elongation measurements were carried out on an UTM4204 mechanical instrument (Shenzhen 3C aspect Technology Co., Shenzhen, China) according to ISO 10810 methods. The cross speed was 20 mm/min. There were five tested specimens for every tested sample. The samples remained in the laboratory at least for 2 days and the room temperature was 20-25 $^{\circ}C$.

The thermal stability of the resins may be assessed by the temperature range of their mass losses measured by thermogravimetry (TG), while the effects of additives on the heat changes during the decomposition can be studied by differential thermal analysis (DTA) and were carried out on a WCT-2 thermal analyzer (Beijing Hengjiu Science Instrument Factory, Beijing, China). TG and DTA were performed under air at a heating rate of 10 $^{\circ}C$ min^{-1} and an air flow rate of 60 mL min^{-1} , $\alpha-Al_2O_3$ was taken as the reference material. The temperature ranged from room temperature to 800 $^{\circ}C$.

The morphology of the additives and the char formed after heating of the samples was investigated by means of scanning electron microscopy (SEM) (Hitachi High-Technologies Co., Japan).

III. RESULTS AND DISCUSSION

A. XRD and TEM Analysis:

The obtained Zn_2SnO_4 products were analyzed by

wide-angle XRD measurement, and the XRD patterns are shown in Figure 1. All of the peaks can be readily assigned to a pure phase of Zn_2SnO_4 [JCPDS 73-1725], which indicated the formation of a homogeneous compound with face-centered cubic structure.

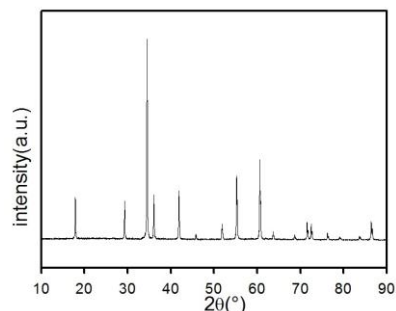


Figure 1. X-ray diffraction pattern of Zn_2SnO_4 products

The images of Zn_2SnO_4 prepared with activated carbon and without activated carbon were shown in Figure 2. The image shows that it is not easy to identify the particle feature of the activated carbon in SEM due to the small size of single carbon particles. The morphology is monolithic on the micrometer scale, with the particles having a coarse surface. On the other hand, the Zn_2SnO_4 sample exhibits a somewhat different morphology compared with its original activated carbon template. Many irregular particles with macropores between them can be easily found in the Zn_2SnO_4 product. This is probably due to fragmentation during carbon combustion due to the lower volume of the Zn_2SnO_4 formed.

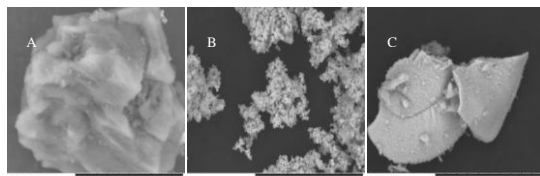


Figure 2. SEM images of (A) activated carbon template and (B) Zn_2SnO_4 prepared with activated carbon as template and (C) Zn_2SnO_4 prepared without activated carbon as template

B. Flame Retardant and Smoke Suppressant Properties

As shown in Table 1, the LOI of the PVC samples increased along with the increase in the corresponding flame retardants. It can be seen that in PVC samples, the flame retardants Zn_2SnO_4 enhance the LOI greatly when incorporated at levels of 5 phr (parts by weight per hundred parts of resin) to 20 phr into the PVC formulation. When the additive level is 20 phr, the LOI for Zn_2SnO_4 prepared without activated carbon as template was 36.4, while the LOI for Zn_2SnO_4 prepared with activated carbon as template can reach to 37.9, about 9 LOI points higher than the neat PVC sample. A comparison of sample II(D) with sample III(D) shows that the LOI of the later was higher than that of the former, and this indicated that the Zn_2SnO_4 prepared with activated carbon as template was better than that of Zn_2SnO_4 prepared without activated carbon as template.

TABLE 1. SOME PROPERTIES OF THE PVC SAMPLES

Sample	Flame retardant	content (parts)	LOI(%)	SDR(%)	MSD(%)	CY(%)	Tensile Strength(MPa)	Elongation(%)
I	black	0	28.7	90.5	100.0	20.8	28.85	228
II (A)		5	33.1	88.3	95.7	23.4	24.51	152
II (B)	Zn ₂ SnO ₄ without	10	34.9	85.8	93.7	26.7	24.90	156
II (C)	AC as template	15	36.0	86.2	93.2	29.7	25.47	168
II (D)		20	36.4	86.4	94.5	29.4	22.52	133
III(A)		5	33.4	86.7	94.9	27.6	22.66	257
III(B)	Zn ₂ SnO ₄ with AC	10	35.2	83.3	90.7	29.5	21.14	245
III(C)	as template	15	36.7	83.1	91.2	28.9	21.48	232
III(D)		20	37.9	84.5	92.8	29.8	21.52	246

That due to the Zn₂SnO₄ which prepared with activated carbon as template particle size small, and have good dispersion in the PVC materials.

As indicated in Table 1, it can be seen that Zn₂SnO₄ can apparently improve the char yield. When the additive level reaches to 20 parts, the anaerobic char yield is 29.4% [Sample II (D)] and 29.8% [Sample III (D)], respectively, and it is 8.6 and 9.0 units higher than that of the neat PVC sample, and it is consistent with their high LOI value. These indicate that Zn₂SnO₄ can improve the LOI and the anaerobic char yield of the non-flame retardant PVC sample at the same time. The reason is that Zn₂SnO₄ could help the PVC sample to form char, and the char covered the surface of the PVC resin and insulated the oxygen and heat to improve the flame-retardant property.

As seen in Table I, the SDR and MSD of the neat PVC was 90.5% and 100%. The SDRs of the samples that were treated with flame retardants are lower than that of the sample of plasticized PVC. For example, Zn₂SnO₄ with activated carbon as template reduced SDR from 90.5% to 83.3% when 10 phr was incorporated. The flame retardants have little effect on the SDR when their content is more than 10 phr. The MSD results are consistent with the SDR results. All of these indicated that Zn₂SnO₄ is a kind of efficient flame retardant and smoke suppressant for PVC.

C. Analysis of Mechanical Property

As shown in Table 1, the tensile strength and elongation at break of neat PVC were 28.85 MPa and 228% respectively. The tensile strength of the PVC samples basically decreased with the increasing addition of the flame retardants, and this may be attributed to the following: First, the effects of the additives on the crystallization and orientation behavior of PVC molecules; Secondly, the effect of the stress concentration [11]. On top of that, the addition of the Zn₂SnO₄ with activated carbon as template increased the elongation of the PVC sample, and this may have been caused by the toughened effect of small particle size additives; moreover, the increment decreased along with the increased addition, and this may be attributed to the increase in the stress concentration with the increase in additives.

D. Thermal Analysis

Figure 3 shows the TG and DTA curves of the PVC samples, and Table 2 shows the corresponding relative parameters, such as the starting decomposition temperature T_{1%} (T_{1%} is the temperature at which the samples decompose

1%), the exothermic peaks, and weight loss.

It can be seen in Figure 3 that the thermal degradation of all the samples occurred in two steps, which were in good agreement with the results reported in the literature [12, 13]. The first degradation step in the temperature range of 200-340 °C could be attributed to the emission of hydrogen chloride and the degradation of DOP. The second degradation step in the temperature range of 400-600 °C owed to the chain scission of carbonaceous backbone and oxidation of the unstable char.

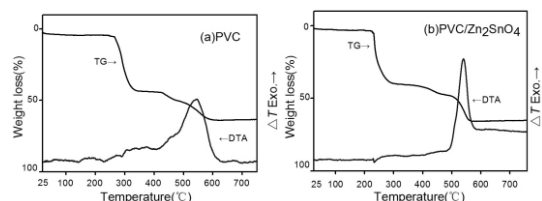


Figure 3. TG and DTA curves of the PVC samples

Figure 3 and Table 2 showed that the weight loss and decomposition temperature range of flame-retarded PVC were significantly different from that of neat PVC. When Zn₂SnO₄ was added to PVC, the weight loss decreased from 65.3% to 57.4%, and the initial decomposition temperature, T_{1%} decreased from 252 °C to 218 °C. All of these findings indicate that the Zn₂SnO₄ catalyze the dehydrochlorination of PVC and promote early crosslinking that leads to rapid charring, thereby decreasing the SDR and increasing the LOI and solid yield of the samples. These results are consistent with the data for LOI, SDR, and the char yield in Table 1.

TABLE 2. TG AND DTA RESULTS OF THE SAMPLES

Sample NO.	T _m (°C)	T _{1%} (°C)	First Stage		Second Stage	
			T _R (°C)	W _L (%)	T _R (°C)	W _L (%)
A	544	252	198~346	65.3	412~608	26.8
B	540	232	218~303	57.4	351~568	34.2

As shown in Figure 3 and Table 2, the DTA curve of the samples treated with the Zn₂SnO₄ presented only an endothermic peak at the first stage and an exothermic peak at the second stage respectively. The temperature of the endothermic peak was higher and that of the exothermic peak was lower than those of the neat soft PVC sample.

E. Analysis of Char Morphology

In order to further understand the role of Zn₂SnO₄

additives to PVC, the surface morphology of the char residue was investigated by using SEM (Figure 4).

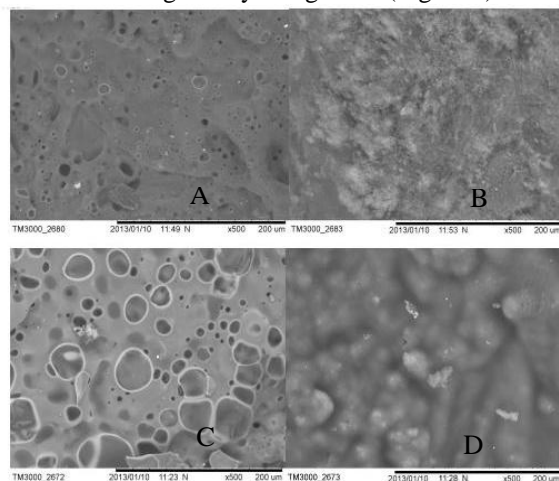


Figure 4. SEM micrographs of the char(A/B-The inner/outer surface of char from neat PVC; C/D- The inner/outer surface of char from PVC with 15phr Zn_2SnO_4)

For the outer surface, the morphology of the char formed from neat PVC shows a cindery structure, while the morphology of the char formed from PVC containing the flame retardants shows a densified structure. The densified structure can form a barrier to inhibit both the transfer of combustible gases to the vapor phase and the transfer of heat energy to the PVC bulk, a situation which is beneficial to flame retardant improvement.

For the inner surface, the neat PVC showed a compact structure with few pores, while the morphology of sample containing 20 phr Zn_2SnO_4 displayed an alveolate and a breakable structure. Perhaps, most of the heat and flammable volatiles could hardly penetrate the stable char layer into the flame zone during the combustion in the presence of Zn_2SnO_4 .

IV. CONCLUSIONS

Face-centred cubic structure Zn_2SnO_4 had been prepared from precursor calcination method use activated carbon as template, based on the extensive analysis conducted in this study, it could be concluded that Zn_2SnO_4 additives could act as efficient flame retardants and smoke suppressants for flexible PVC. In particular, the LOI of PVC/ Zn_2SnO_4 increased from 28.7% to 37.9% and the SDR value was as low as 84.5%. Also, Zn_2SnO_4 has little influence on the tensile property of the PVC samples. It can greatly improve the elongation. The thermal degradation of flexible PVC

was described by TG-DTA in air, the thermal analysis results showed that Zn_2SnO_4 enhances the stability of the residual char, and promotes the dehydrochlorination of PVC during thermal decomposition, thus the flame-retardant and smoke-suppressant properties are improved.

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