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Synergistic effects of inorganic tin compounds and Sb_2O_3 on thermal properties and flame retardancy of flexible poly(vinyl chloride)

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ABSTRACT

The effects of inorganic tin compounds such as zinc hydroxystannate (ZHS), tin dioxide (SnO_2), and tin monoxide (SnO), Sb_2O_3, and their mixtures on the flame retardant and smoke suppressant properties of flexible poly(vinyl chloride) (PVC), and their flame retardant and smoke suppressant actions, were studied using the limiting oxygen index (LOI) test, the smoke density rating (SDR) test, thermogravimetric analysis/differential thermogravimetry/differential thermal analysis (TGA/DTG/DTA), scanning electron microscopy (SEM), and quantitative analysis. The results showed that the incorporation of small amounts of inorganic tin compounds and their mixtures with Sb_2O_3 can increase the LOI of PVC and decrease the SDR during combustion. Partial replacement of Sb_2O_3 in flexible PVC by ZHS resulted in a significant synergistic improvement in flame retardant behavior. TGA/DTG/DTA, SEM, and quantitative analysis showed that ZHS acts as a flame retardant in the solid phase, Zn^{2+} can catalyze dehydrochlorination of PVC and promote early cross-linking, leading to rapid charring, and Sn^{4+} can react with the char, thereby increasing the char stability. These actions, combined with the vapor-phase role of Sb_2O_3, can significantly enhance the flame retardancy of PVC.

1. Introduction

Poly(vinyl chloride) (PVC) is extremely useful as a commercial material. Among the thermoplastics, it ranks second only to polyolefin in total worldwide production volume [1]. However, for many applications, an organic plasticizer such as dioctyl phthalate (DOP), filled at various levels, is needed to make PVC materials flexible and easy to process [2–4]. However, this also makes ignition and burning of PVC products easier. As PVC is used for decoration and for building materials, it is essential to make it flame retardant.

A large number of chemical compounds have been reported to be flame retardant and smoke retardant for PVC. These compounds include alloys, inorganic compounds, coordination compounds, and organic compounds [5]. Antimony compounds, especially Sb_2O_3 and Sb_2O_5, are good flame retardants for PVC and are widely used, but antimony compounds can produce toxic or irritating vapors under combustion conditions [6,7]. In addition, antimony compounds are toxic and carcinogenic, and can cause diseases of the liver, skin, and respiratory and cardiovascular systems; excessive amounts of antimony may cause acute cardiac diseases [8,9]. The toxicity of antimony depends on its chemical form: the toxicity of organic antimony compounds is lower than that of inorganic antimony compounds, and the toxicity of Sb(V) is lower than that of Sb(III); SbH_3 and Sb_2O_3 have the highest toxicities [10]. Little work has been done on the ecotoxicity of antimony compounds, as they are not widely present in the environment. Further work needs to be done on the physiological toxicity and ecotoxicity of antimony compounds [11]. Recently, inorganic compounds such as zinc hydroxystannate (ZHS) and zinc stannate (ZS) have been widely developed as flame retardants because of their lower toxicities. The incorporation of ZHS in plastics is unlikely to present an environmental hazard at any stage of its use. In the event of a spillage before processing, the low vapor pressure and low water solubility of ZHS suggest that it would not readily enter environmental systems. It has been reported that ZHS and ZS can be used as highly effective flame retardants [12,13]. The advantages of using ZHS and ZS as flame retardants are that they generate lower quantities of smoke and are less toxic than antimony compounds [14].

The aim of this research was to study the synergistic effects of using ZHS and Sb_2O_3 in flexible PVC. The action of ZHS as a flame retardant for flexible PVC, compared with those of SnO_2, SnO, and ZnO, was studied by thermogravimetric analysis/differential thermogravimetry/differential thermal analysis (TGA/DTG/DTA), scanning electron microscopy (SEM), and elemental analysis.

2. Experimental

2.1. Materials

The materials used were PVC SG5 (Beijing Second Chemical Co., Beijing, China); dioctyl phthalate (DOP) as a plasticizer (Shanghai

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Dongfang Chemicals Co., Shanghai, China); an organic tin compound, namely diisooctyl-2,2′-[(dioctylstannylene)bis(thio)]diacetate, as a heat stabilizer, and calcium stearate as a lubricant (Hebei Baoding Chemical Co., Baoding City, China); ZnO (Tianjin Beifang Tianyi Chemical Co., Tianjin, China); SnO_2 and SnO (Beijing Shuanghuan Chemical Co., Beijing, China); NaOH (Tianjin Beifang Huabo Chemical Co., Tianjin, China); $ZnSO_4 \cdot 7H_2O$ (Tianjin Third Chemical Co., Tianjin, China); $Na_2Sn(OH)_6$ (Tianjin Third Chemical Co., Tianjin, China); and Sb_2O_3 (Beijing Xudong Chemical Co., Beijing, China).

2.2. Preparation of flame retardant and PVC samples

The flame retardant ZHS was prepared as previously described [15].

Samples were prepared by mixing PVC with DOP, a heat stabilizer, a lubricant, a coupling agent, and a flame retardant, and then blending in a two-roll mill at 170 °C for 10 min, followed by compression at 180 °C to form sheets of dimensions 100 mm × 50 mm × 3 mm. Test specimens were cut from the molded sheets. The basic recipe for all of the samples was as follows: PVC 100 parts, DOP 40 parts, stabilizer 3 parts, calcium stearate 0.5 parts, stearic acid 0.5 parts, and some flame retardant.

2.3. Measurements and characterization

The flame retardancy of plastic materials can be determined by many methods, such as thermal analysis, tunnel flame-spread tests, limiting oxygen index (LOI), smoke production tests, and analysis of solid residues or the gaseous products of thermal decomposition [16]. The LOI value is the minimum amount of oxygen in an oxygen–nitrogen mixture required to support combustion over 3 min or until the specimen is consumed for more than 5 cm from the top. The LOI method is a simple, convenient, fast, and effective method of studying the flame retardancy of plastic materials. In this research, the flame retardancies of plastic materials were measured using the LOI. LOI values were determined in accordance with ASTM D2863-2000 using a General Model HC-2 LOI instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China).

The smoke density ratings (SDR) of samples in the form of plates measuring 25.3 mm × 25.3 mm × 3 mm were determined in accordance with ASTM D 2843-1993 using a General Model JCY-1 instrument (Nanjing Jiangning Analysis Instrument Factory, Nanjing, China). The method consists of measuring the light absorption rate of the smoke in the initial period of a burning time of 4 min. A special smoke chamber made of heat-insulated material, of internal dimensions (750 mm × 750 mm × 1000 mm) ± 5 mm, was used. The chamber was equipped with an ignition system, an illuminance-measuring system, and a ventilation system.

Thermal analysis (TGA, DTG, and DTA) was carried out on a DT-40 analyzer (Shimadzu Corp., Kyoto, Japan) under air at a heating rate of 10 °C min^{-1} and an air following rate of 60 mL min^{-1}. The temperature range was from room temperature to 800 °C.

The morphologies of the chars formed after combustion of the samples were investigated by SEM (SEM-KYKY-2800B, Chinese Academy of Sciences Instrument Factory, Beijing, China). The char surfaces were covered with gold before observation.

3. Results and discussion

3.1. Flame retardancy and smoke suppression

From the data presented in Table 1, it can be seen that Sb_2O_3, ZHS, and their mixtures are good flame retardants for flexible PVC. The LOI values of the samples increase with increasing amounts of flame retardant. A small amount of flame retardant can greatly enhance the LOI. The LOI values of the samples containing Sb_2O_3/ZHS (1:1, weight ratio) are higher than those of the samples treated with Sb_2O_3 or ZHS alone, which indicates that Sb_2O_3 and ZHS have a good synergistic effect on the flame retardancy of flexible PVC.

Table 1
Effectiveness of additives for flame retardancy and smoke suppression in PVC.

Sample	Flame retardants	Content/phr	LOI/%	SDR/%	EFF	SE1[a]	SE2[b]
1	Sb_2O_3	5	30.8	–	1.68	–	–
2	Sb_2O_3	10	31.6	–	0.992	–	–
3	Sb_2O_3	15	33.1	84.06	0.843	–	–
4	ZHS	5	29.3	–	1.23	–	–
5	ZHS	10	30.1	–	0.760	–	–
6	ZHS	15	31.6	71.54	0.683	–	–
7	Sb_2O_3/ZHS (1:1)	5	31.7	–	1.95	1.16	1.59
8	Sb_2O_3/ZHS (1:1)	10	34.3	–	1.41	1.42	1.86
9	Sb_2O_3/ZHS (1:1)	15	40.4	74.74	1.62	1.92	2.37
10	ZnO	15	26.3	86.10	0.117	–	–
11	SnO_2	15	30.6	74.21	0.576	–	–
14	SnO	15	31.4	71.22	0.661	–	–
12	ZnO/Sb_2O_3 (1:1)	15	31.4	84.03	0.661	0.784	5.65
13	SnO_2/Sb_2O_3 (1:1)	15	32.1	73.99	0.736	0.873	1.28
15	SnO/Sb_2O_3 (1:1)	15	32.3	74.83	0.757	0.898	1.145
16	–	–	25.2	84.24	–	–	–

[a] SE1is on the base of Sb_2O_3.
[b] SE2 is on the base of the other compound of the mixture.

ZHS contains Zn^{2+} and Sn^{4+}, so the PVC samples were treated with ZnO, SnO_2, SnO, and ZHS, respectively, to compare and study the actions of Zn^{2+} and Sn^{4+} in the PVC samples. The results show that ZnO can enhance the LOI marginally compared with that of a pure PVC sample; SnO_2 or SnO can greatly increase the LOI, which is similar to the result obtained with ZHS. However, there is no synergism between the metal oxides and Sb_2O_3, which is different from the result obtained with Sb_2O_3/ZHS.

The flame retardant efficiency (EFF) and the synergistic efficiency (SE) [17] were calculated from

$$EFF = \Delta LOI(\%)/FR(\%) \quad (1)$$

where ΔLOI is the change in the LOI and FR is the flame retardant content; EFF is a dimensionless quantity. The higher the EFF, the greater the efficiency of the flame retardant.

$$SE = EFF_1/EFF_2 \quad (2)$$

where EFF_1 is the flame retardant efficiency of the synergistic system, and EFF_2 is the flame retardant efficiency of a single flame retardant. SE is also a dimensionless quantity. It can be used to reflect the synergistic efficiency of two or more flame retardants.

The EFF and SE data are listed in Table 1. As indicated in Table 1, Sb_2O_3 is a highly effective flame retardant for flexible PVC. This is mainly because Sb_2O_3 can react with HCl to form volatile antimony chloride, which scavenges flame-propagating radicals; the efficiency of Sb_2O_3 is higher than that of ZHS. There is good synergism between Sb_2O_3 and ZHS (SE1 and SE2 are higher than 1, indicating that the LOI of the sample treated with Sb_2O_3/ZHS is higher than those of samples treated separately with Sb_2O_3 or ZHS). The two species act on the flexible PVC synchronously, which can greatly enhance the flame retardancy of PVC compared with that of a single flame retardant system. The EFF of ZnO is close to zero, indicating that no flame retardancy is imparted by ZnO. The EFFs of SnO_2 and SnO are similar to that of ZHS, but SE1 is less than 1, which shows that the LOI values of the samples treated with ZnO/Sb_2O_3, SnO_2/Sb_2O_3, or SnO/Sb_2O_3 are lower than that for those treated with Sb_2O_3 alone. It was therefore concluded that Sb_2O_3/ZHS is the most effective of these flame retardants for flexible PVC.