Cone Calorimetric Study of Gangue Flame Retardance of PVC

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Abstract: Gangue as flame retardant was used to flexible poly (vinyl chloride) (PVC), and the flame retardant properties of PVC were investigated by the limiting oxygen index, and cone calorimeter tests (CONE). The CONE result indicated that the rate of heat release (HRR) and total heat release (THR) of PVC treated with flame-retardants were decreased, a more compact char residue formed on the surface of the sample with gangue of the sample during the combustion process. And the smoke production rate (SPR) and total smoke produced (TSP) were increased compared with that of pure PVC. Besides, PVC treated with gangue and Sb_2O_3 showed a high limiting oxygen index, high decomposition temperature, which indicated that the flame retardance of the treated PVC was improved.

Introduction

PVC materials or products tend to have excellent fire performance. But to make it easy to process, semirigid and flexible PVC compound always contains a large volume of plasticizer such as DOP [di(2-ethylhexyl)phthalate], which can deteriorate the flame retardation and smoke suppression properties. When the PVC products contain 45 parts DOP, the limiting oxygen index (LOI) would decrease to about 24 and the PVC would thus become a high-flammability material. However, plasticized PVC products can still have good fire performance, particularly if additionally fire-retarded [1].

In recent years, many types of chemical compounds have been reported as flame retardants and smoke suppressants for flexible PVC, including metal alloys, inorganic compounds, coordination compounds, and organic compounds. Sb_2O_3 is one of the important inorganic flame retardant, as a synergistic agent added to the flame retardant polymeric materials containing halogen flame retardant, widely used in plastic products, rubber, textile fabric, coating and polymer materials [2]. Because of the high loading it is essential that good degree of flame retardancy be obtained, but mechanical properties decrease obviously. Using coupling agents and synergists are good ways to solving this problem [3–5]. Many elements, such as alloys, organic substances and inorganic compounds including antimony, tin, zinc, copper, iron and molybdenum, have been used in the flame retardation and smoke suppression of PVC. Gangue contains many kinds of metal oxides, which may have the similar effective.

The purpose of our present study is to study flame retardant, smoke suppressant of the samples treated with gangue.

Experimental

Materials

PVC (SG2, Beijing chemical factory Co., Ltd); dioctyl phthalate (DOP) (Tianjin east China reagent factory); Sb_2O_3 (industrial grade, Shanghai huigu chemical products Co., Ltd); Tribasic lead sulfate, Dibasic lead phosphate, commercially available; Zinc stearate (industrial grade, Tianjin east China reagent factory).

Preparation of Flame Retardant PVC Samples

Formulation according to predetermined material (including PVC, DOP, tribasic lead sulfate, dibasic lead phosphate, zinc stearate, Sb_2O_3, gangue) are mixed in a mixer 3 to 5 minutes at 35 - 45 ℃. Then the mixture was completely mixed on the two-roll mill at 165℃ for 6-8 min, compressed at 180℃ to form sheets of 100mm×100mm×3mm. The test specimens were then cut from samples of suitable thickness and size for LOI, and cone calorimeter tests. The compositions of all of the samples are listed in Table 1.

Table 1 The composition of the samples

Samples	PVC (g)	DOP (g)	Tribasic lead sulfate (g)	Dibasic lead phosphate (g)	Zinc stearate (g)	Sb_2O_3 (g)	Gangue (g)	Oxygen index (%)
A	100.0	30.0	2.0	2.0	0.5	0.0	0.0	27.6
B	100.0	30.0	2.0	2.0	0.5	7.0	0.0	35.6
C	100.0	30.0	2.0	2.0	0.5	6.5	0.5	34.9
D	100.0	30.0	2.0	2.0	0.5	6.0	1.0	34.8
E	100.0	30.0	2.0	2.0	0.5	5.5	1.5	35.0
F	100.0	30.0	2.0	2.0	0.5	5.0	2.0	34.8
G	100.0	30.0	2.0	2.0	0.5	4.5	2.5	34.6
H	100.0	30.0	2.0	2.0	0.5	4.0	3.0	34.5
I	100.0	30.0	2.0	2.0	0.5	3.0	4.0	32.9

Characterization

The limiting oxygen index (LOI) test was performed with a JF-3 oxygen index test instrument (Jiangning Analytical Instrument Factory, China) in terms of the standard LOI test, ASTM D2863-2000.

Cone calorimeter measurements were performed at an incident radiant flux of 50 kw m^{-2}, according to ISO 5660 protocol. The samples (100 mm × 100 mm × 3 mm) were laid on a horizontal sample holder.

Results and discussion

Flame retardancy of Sb_2O_3 and gangue

The flame-retardant properties of PVC upon the addition of the different flame-retardants were evaluated in terms of LOI. The detailed results were summarized in Table 1.

Sb_2O_3 is good for flame retardant effect of PVC material, it is in the gas phase and condensed phase also play a role, so better flame retardant effect, used in plastics and rubber industry, attracted wide spread attention. To reduce the use of Sb_2O_3, while get better flame retardancy for PVC, gangue was added.

Table 1 listed the related LOI data obtained from different addition of Sb_2O_3 and gangue in PVC. The LOI data presented a trend of ‘‘decay-increase-maximum-decay’’, with the increase of the gangue content and the decrease of the Sb_2O_3 content in the formulation. The results also showed that the highest LOI value of sample E with 1.5 phr gangue was 35.0 %. These results indicated that the addition of a suitable amount of Sb_2O_3 and gangue could increase the flame-retarding of PVC.

Cone calorimeter test

Cone calorimeter is one of the most useful bench-scale tests that attempt to simulate real-world fire conditions, providing a wealth of information on the combustion behavior [6, 7]. Some cone calorimeter results have been found to correlate well with those obtained from largescale fire tests and can be used to predict the behavior of materials in real fires [8].

Heat release rate (HRR)

The changes in HRR as a function of burning time for different PVC samples are shown in Fig.1. It can be seen that the peak HRR values of sample A, sample B and sample E are 97.8, 21.4, and 23.3 kW m^{-2}, respectively. That is to say, the addition of gangue can dramatically decrease the peak HRR value, and the HRR value of sample E containing 5.5 phr Sb_2O_3 and 1.5 phr Sb_2O_3 decreased rapidly from 97.8 to 23.3 kW m^{-2} of sample A. Moreover, the time to peak HRR (tPHRR) of sample A, sample B and sample E are 331, 626, 578 s, respectively. The flame retarded PVC with gangue was later by 247 s than pure PVC.

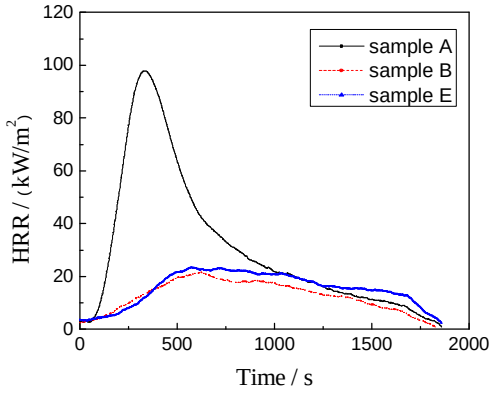

Fig.1 HRR curves of samples

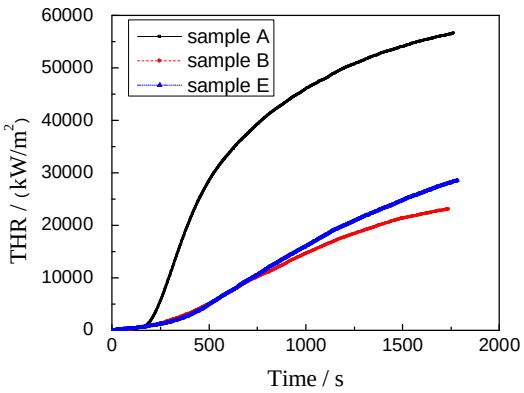

Fig.2 THR curves of samples

Total heat release (THR)

Corresponding to the HRR curve, the total heat release (THR) curves of the PVC samples are shown in Fig.2. It is reported that the slope of THR curve can be assumed as representative of flame spread [9].

As we can see, the slope of sample A is the biggest one, indicating that the fire spreads of sample A is the quickest among all samples. Comparing sample E with sample A, the THR of sample E is much lower than that of sample A, which is due to the fact that the char layer of sample E is more compact than that of sample A. These results are probably because the residual char undergoes slow glowing combustion, such that the THR value gradually increases until the end of the test.

Smoke production rate (SPR) and total smoke produced (TSP)

As shown in Figs.3 and 4, the smoke production rate (SPR), and total smoke produced (TSP) are accurate indicators of the smoke generated during combustion. It can be seen that the addition of gangue without effect in suppress the SPR and TSP of PVC.

As shown in Fig.3, the peak SPR value of sample E (0.188 m^2 s^{-1}) is the largest one among all the samples, the peak SPR value of sample A and sample B are 0.178 m^2 s^{-1} and 0.157 m^2 s^{-1}, respectively, which indicate that the smoke suppression ability of PVC no improve with the gangue as flame retardant added. It can be seen from Fig.4 that the TSP value of sample E also higher than sample A. But, PVC with gangue produce smoke earlier than sample A, indicating that it decomposes earlier than sample A, which is corresponded with HRR and THR curves.

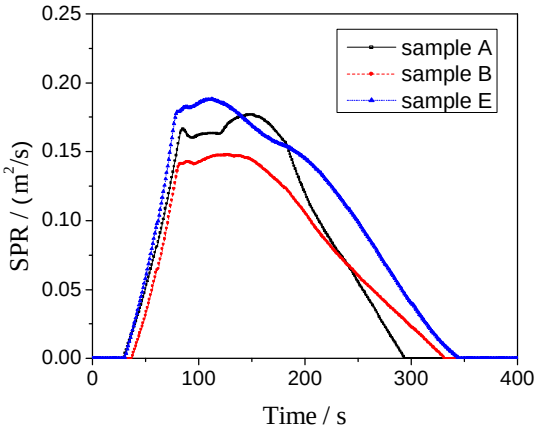

Fig.3 SPR curves of samples

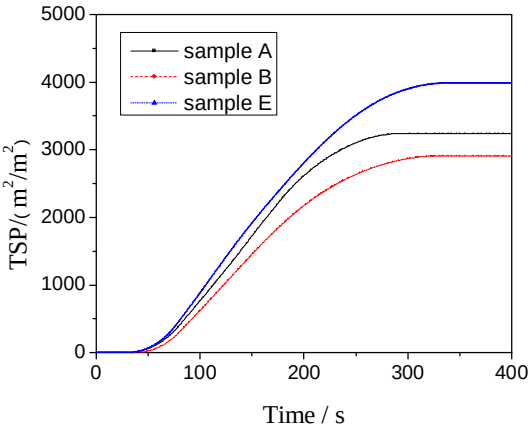

Fig.4 TSP curves of samples

Conclusions

LOI studies showed that gangue had a good flame retarding effect with Sb_2O_3, a suitable amount of gangue could greatly increase the LOI. When 1.5 phr gangue and 5.5 phr Sb_2O_3 was added to PVC, the LOI value was the maximum. Cone calorimeter data show that the addition of gangue can reduces the heat release rate and total heat release in flame-retardant PVC, a more compact char residue formed on the surface of the sample with gangue of the sample during the combustion process. Hence, gangue has the good excellent flame retardant effect on PVC.

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