

Montmorillonite as Flame Retardant for Flexible Poly (Vinyl Chloride)

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Abstract: Montmorillonite as flame retardant was used to flexible poly (vinyl chloride) (PVC), and the flame retardant and smoke suppressant properties of PVC were investigated by the limiting oxygen index, smoke density rating, and cone calorimeter tests (CONE), the thermal degradation behaviors of PVC were studied by thermogravimetric analysis (TG) in nitrogen atmosphere. The mechanical properties testing resultant data show that montmorillonite better effect on the tensile strength of the sample. The CONE result indicated that montmorillonite can reduce the heat release rate in flame-retardant PVC: a more compact char residue formed on the surface of the sample with montmorillonite of the sample during the combustion process. The TG result showed that the sample with montmorillonite has higher thermal stability than pure PVC. Besides, PVC treated with montmorillonite and Sb₂O₃ 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 [2]. Sb₂O₃ 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 [3]. 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 [4-6]. 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.

Montmorillonite contains many kinds of metal oxides, which may have the similar effective. The purpose of our present study is to study mechanical properties, flame retardant and smoke suppressant of the samples treated with montmorillonite.

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

The test samples were prepared as follows: first, the samples were prepared by melting and mixing PVC with DOP, tribasic lead sulfate, dibasic lead phosphate, zinc stearate, and a certain amount of the flame retardant prepared in this study. Subsequently, the specimens were blended in a two-roll mill at 165°C for 6-8 min, followed by compression at 180°C to form sheets of 100mm×100mm×3mm. The test specimens were then cut from samples of suitable size for mechanical properties, LOI, SDR, and cone calorimeter tests. The basic formula was PVC: 100 parts per hundreds of resin (phr), DOP: 30 phr, tribasic lead sulfate: 2 phr, dibasic lead phosphate: 2 phr, zinc stearate: 0.5 phr, and the actual amounts of flame retardant are given in Table 1.

Table 1 The flame retardant content of the samples

Sample	1	2	3	4	5	6	7	8	9	10	11
Montmorillonite / phr	-	-	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0
Sb_2O_3 / phr	-	7.0	6.5	6.0	5.5	5.0	4.5	4.0	3.0	2.0	1.0

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. The mechanical properties were tested according to GB/T 1040.2-2006 standard with a LJ-5000 tensile testing machine (Chengde Experimental Factory). At least five specimens were tested for each sample and the average values were reported. Thermo-gravimetry (TG) was carried out on a HCT-2 thermal analyzer (Beijing Hengjiu Scientific Instrument Factory) under a dynamic nitrogen (dried) atmosphere at a heating rate of 10°C min⁻¹, 4 mg samples were heated from room temperature to 800°C. 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

LOI and SDR analysis

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 get better flame retardancy for PVC, montmorillonite was added.

Table 2 LOI and SDR results of the samples

Sample	1	2	3	4	5	6	7	8	9	10	11
LOI/%	27.6	35.6	33.7	33.9	33.9	34.1	33.8	33.3	33.0	31.9	30.8
SDR/%	82.7	87.9	85.3	84.3	81.4	79.5	78.3	72.1	81.3	81.7	82.8

Table 2 listed the related LOI and SDR data obtained from different addition of Sb_2O_3 and montmorillonite in PVC. The LOI data presented a trend of “increase-maximum-decay”, and the

SDR data decreased to a minimum value and then increased with the increase of the montmorillonite content and the decrease of the Sb_2O_3 content in the formulation.

It can be seen that the LOI value of samples 3–11 were slightly lower than sample 2 but much higher than sample 1. And the highest LOI value of sample 6 with 2 phr montmorillonite was 34.1 %. The results obtained from the SDR tests also showed that sample 3–8 gradually decreased, the highest SDR value of sample 8 containing 3 phr montmorillonite decreased from 82.7 to 72.1 % of sample 1. These results indicated that the addition of a suitable amount of Sb_2O_3 and montmorillonite could increase the flame-retarding and smoke-suppressing of PVC.

Mechanical Properties of flexible PVC

Fig.1 shows the effect of the montmorillonite on tensile strain of samples, which shows that the tensile strain decrease when the added montmorillonite's addition is less than 2 phr, then increase when it is more than 2 phr. So in a certain range, with the added of montmorillonite, the tensile strength of the samples have slightly change, the application scope of samples is not affected.

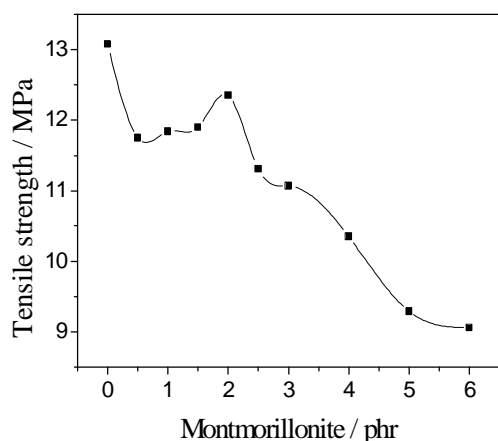


Fig.1 Tensile strength of samples

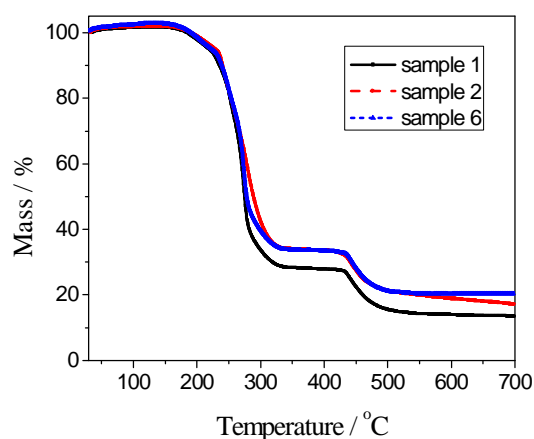


Fig.2 TG curves of samples

Thermal properties of flexible PVC

Figure 2 shows the TG curves of sample 1, sample 2 and sample 6 were carried out in dynamic nitrogen from ambient temperature to 750°C. It can be seen from Fig.2 that all the PVC have three main decomposition processes [7]. The first stage is mainly due to the emission of hydrogen chloride and the degradation of DOP. The second stage is where the carbonaceous backbone suffers chain scission and thus most lower molecular weight compounds (and smoke) are produced. The third stage tends to be, just as for many other polymers, a very slow reaction.

And the initial decomposition temperatures (5.0 mass% mass loss) of them are 218.9, 219.9 and 222.8°C, respectively, which indicate that pure PVC decompose earlier than that PVC added flame retardant, and the initial decomposition temperatures become longer with the increase of montmorillonite content. Additionally, it can be seen form Fig.2 that the char residues at 700°C for sample 1, sample 2 and sample 6 are 12.8, 17.1, and 20.4 mass%, respectively. The increase of char yields agrees with mechanism of flame retardant. Introduction of flame-retardants leads to more char formed at the expense of flammable volatile products of thermal degradation, thus suppressing combustion and increasing the LOI.

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 [8].

The changes in HRR (Heat release rate) as a function of burning time for different PVC samples are shown in Fig.3. It can be seen that the peak HRR values of sample 1-2 and sample 6 are 97.8, 21.4, and 26.7 kW m⁻², respectively. That is to say, the addition of montmorillonite can dramatically decrease the peak HRR value. Moreover, the time to peak HRR (tPHRR) of sample 1, sample 2 and sample 6 are 331, 626, 585 s, respectively. The flame retarded PVC with montmorillonite was later by 254 s than pure PVC, and the sample 2 with only 7 phr Sb₂O₃ was later by 295 s than pure PVC.

Corresponding to the HRR curve, the total heat release (THR) curves of the PVC samples are shown in Fig.4. As we can see, the slope of sample 1 is the biggest one, indicating that the fire spreads of sample 1 is the quickest among all samples. Comparing sample 6 with sample 1, the THR of sample 6 is much lower than that of sample 1, which is due to the fact that the char layer of sample 6 is more compact than that of sample 1.

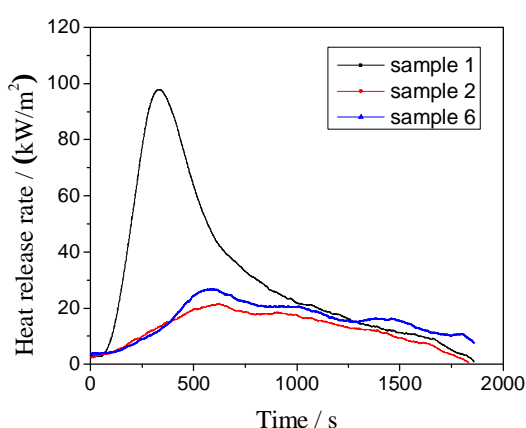


Fig.3 HRR curves of samples

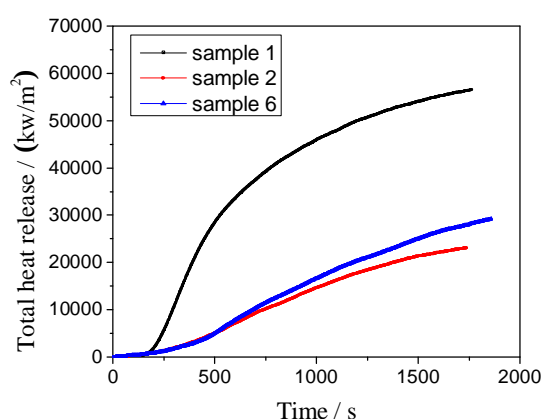


Fig.4 THR curves of samples

Conclusions

LOI and SDR studies showed that montmorillonite had a good flame retarding effect with Sb₂O₃, a suitable amount of montmorillonite could greatly increase the LOI and significantly decrease the SDR. Mechanical test show that montmorillonite has slightly effect on the mechanical properties of the sample in a certain range. Cone calorimeter data show that the addition of montmorillonite can reduces the HRR and THR in flame-retardant PVC. The TG data show that samples with montmorillonite have higher char residues than pure PVC, and the initial decomposition temperature become longer with the increase of montmorillonite content. Hence, montmorillonite has the good mechanical properties and excellent flame retardant effect on PVC.

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References

- [1] Hirschler, M.M. (1982). Recent Developments in Flame-Retardant Mechanisms, Development in Polymer Stabilisation, Applied Science Publ, London. Vol. 5, p. 107.
- [2] Deka BK, Maji TK. (2011). Study on the properties of nanocomposite based on high density

- polyethylene, polypropylene, polyvinyl chloride and wood. *Compos Part A*.42:686–93.
- [3] Rodolfo A Jr, Mei LHI. (2010). Metallic oxides as fire retardants and smoke suppressants in flexible poly(vinyl chloride). *J Appl Polym Sci*.118:2613–23.
- [4] Ren XJ, Song CG, Gao M. (2014). Coal Ash as Flame Retardants for Flexible Poly (Vinyl Chloride), *Advanced Materials Research*. 1056, 62-65.
- [5] Pearce, E.M. (1986). Flame Retardants for Polymer Systems, *Pure & Appl. Chem.*, 58: 925.
- [6] Qu HQ, Wu WH, Jiao YH, Xu JZ. (2005). Thermal behavior and flame retardancy of flexible poly(vinyl chloride) treated with Al(OH)₃ and ZnO. *Polym Int*. 54:1469–73.
- [7] Hirschler, M.M. (1986). Thermal Decomposition (STA and DSC) of PVC Compounds Under a Variety of Atmospheres and Heating Rates, *Eur. Polym. J.*, 20: 710.
- [8] Jiao CM, Chen XL. (2010). Synergistic flame retardant effect of cerium oxide in ethylene-vinyl acetate/aluminum hydroxide blends.*J Appl Polym Sci*.116:1889–93.